FINAL REPORT

PROJECT NO. A-1240

DEVELOPMENT OF MICROCIRCUITS FOR SPACE APPLICATIONS

By L. N. Tharp

Prepared for

NASA Marshall Space Flight Center

Contract No. NAS8-25667

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Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

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FOR SPACE APPLICATIONS

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I. INTRODUCTION

The work described herein was performed under Contract No. NAS8-25667 with the NASA Marshall Space Flight Center. The purpose of this program was (1) to investigate the application of Auger electron spectroscopy as an analytical method for detecting impurities introduced during processing of semiconductor devices and (2) to explore the correlation between surface contamination and selected device parameters in silicon devices.

The program consisted of examining a number of silicon wafers selected from various stages of device processing with Auger spectroscopy and correlating these data with known factors in the device manufacturing process as well as electrical measurements of device performance after several key process steps. These sample wafers were provided by a major manufacturer of silicon power transistors while measurements were carried out in the laboratories of the Physical Sciences Division at Georgia Tech.

The results obtained in this study are discussed in the remainder of this report. Section II briefly describes the techniques and systems utilized in this study. Section III presents a summary of the first phase of the investigation which was aimed at applying Auger spectroscopy to typical process steps to determine difficulties in analysis to be encountered; the following section presents in more detail the data obtained from 50 samples examined at process steps as indicated. Finally, in Section V, conclusions and recommendations are discussed.

II. EXPERIMENTAL SYSTEM AND TECHNIQUES

The experimental system used in these studies consisted of a large bell-jar type ultra-high vacuum system equipped with a spherical retarding field electron energy analyzer for generating the Auger spectra and a special multiple sample turret assembly for sequentially analyzing five wafer type samples.

The vacuum chamber was evacuated by a combination of a Welch 270 l/s Turbo Molecular pump and a Varian 450 l/s noble gas Vac Ion pump with auxiliary titanium sublimation. This system combined the features of fast pumping from atmospheric pressure for rapid cycling and the clean, low ultimate pressure associated with ion pumped systems. Typically, following the introduction of five samples, the system is roughed out mechanically until the Turbo pump can be started. The Turbo pump quickly reduces the system pressure to the 10^{-7} Torr range at which point the Turbo pump is valved off from the system and the Ion pump valved in. This causes a further rapid reduction in system pressure with total pumpdown time from atmosphere to the 10^{-9} Torr range of less than three hours. System ultimate with no baking is 1×10^{-10} Torr. Both ultimate pressure and pumpdown time are improved considerably with occasional mild baking of the system, but such was not warranted for most measurements. This system is shown in Figure 1.

To facilitate the rapid analysis of a number of samples, it was necessary to design a special sample holder which is shown in Figure 2. This holder provides for handling five wafer type samples ranging in diameter from 1 to 1 1/4 inches. (Smaller or larger samples may also be accommodated with minor modifications). Each sample is isolated both electrically and thermally from the other

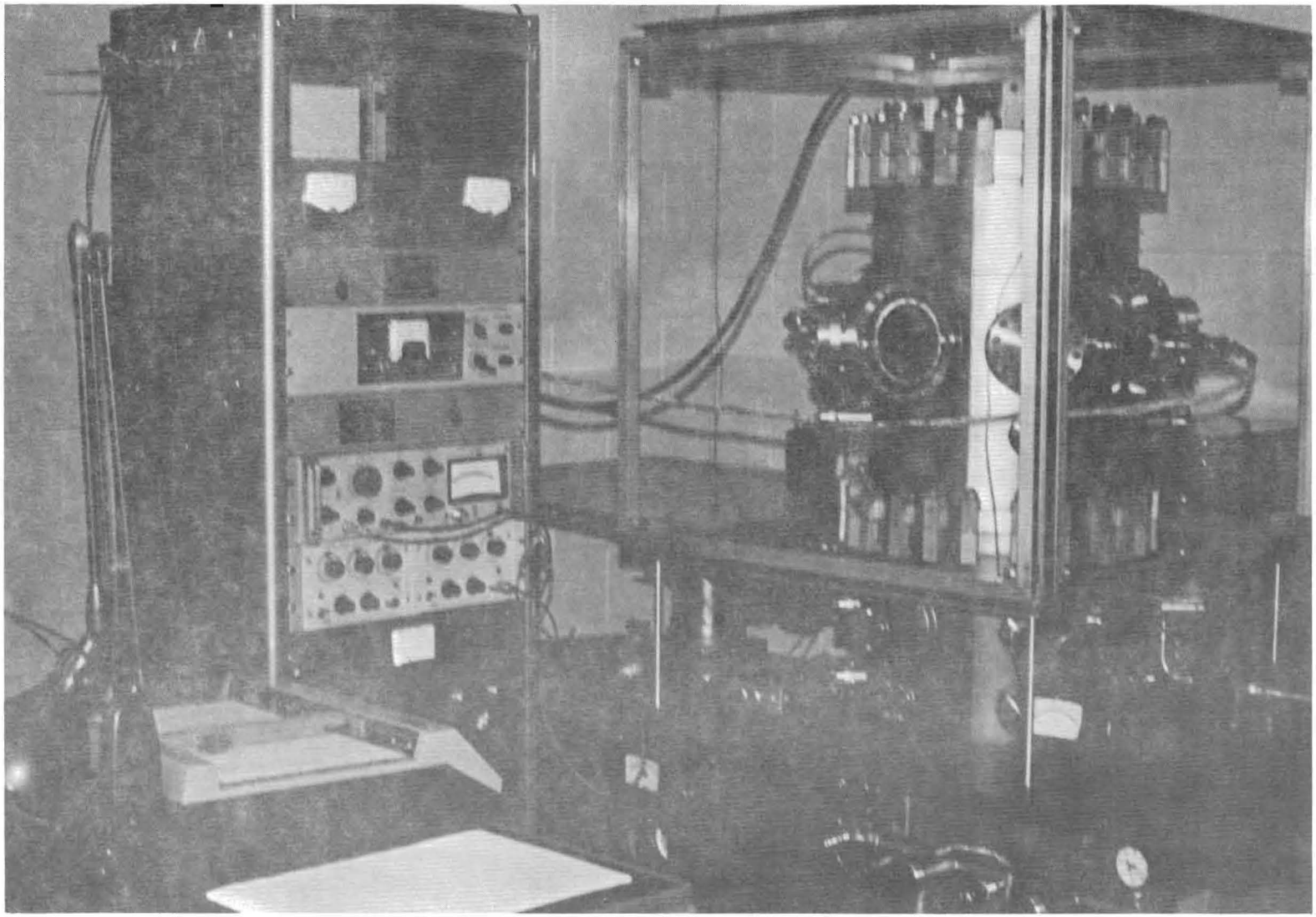

Figure 1. Auger Spectrometer System.

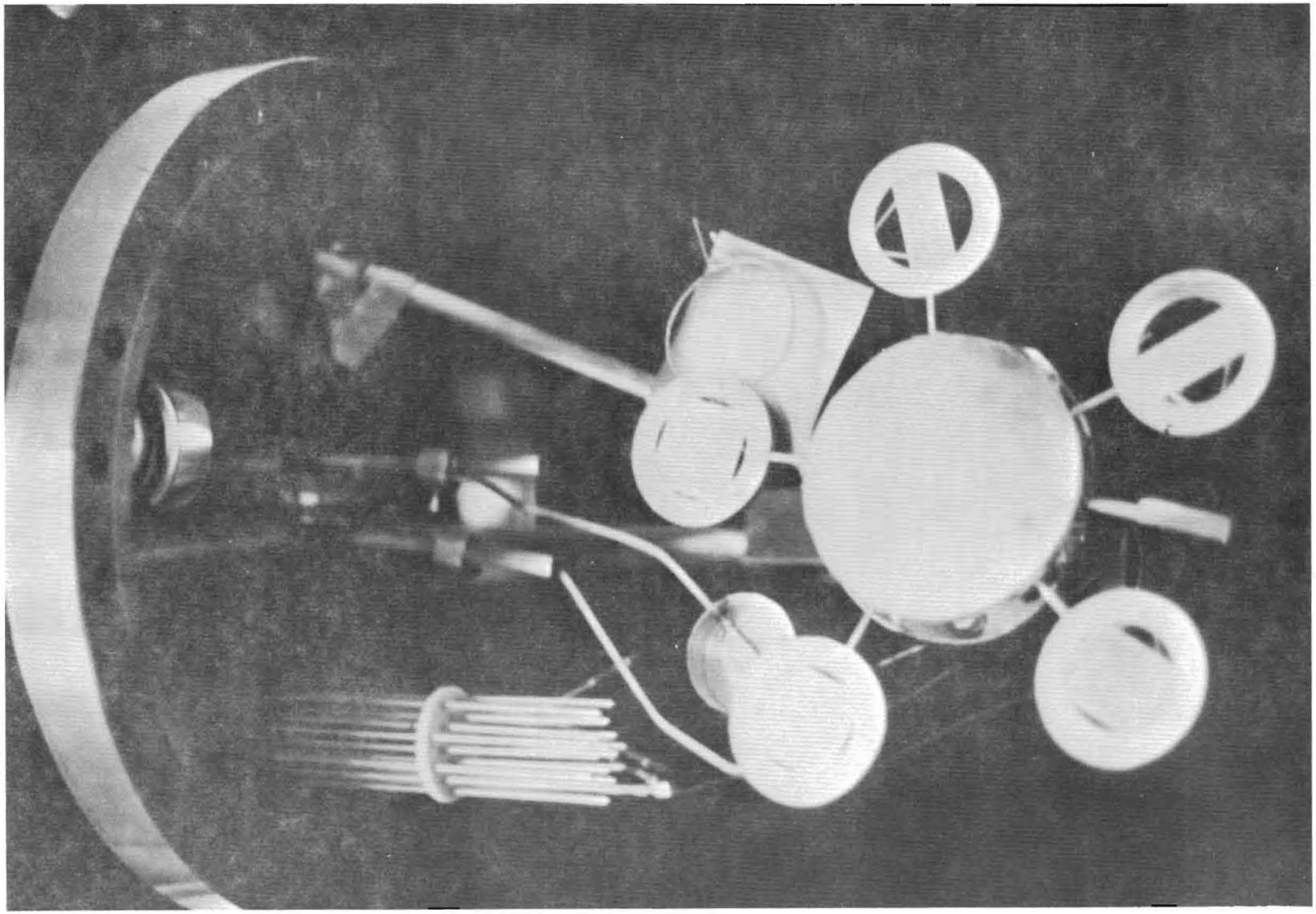

Figure 2. Sample Turret for Five Samples.

samples. The sample turret can be rotated so that each of the five samples can be moved into a number of different positions providing for Auger analysis, indirect electron bombardment heating and RF-DC sputtering for sample cleaning. Electrical contact to the samples is accomplished through a selector switch arrangement near the center of the sample turret.

To generate the Auger spectrum for chemical analysis, the sample is bombarded by a beam of moderate energy primary electrons (50 microamps at 1 to 3 kev). The primary electrons ionize impurity atoms near the surface by removing electrons from the lower lying energy levels. An empty level is filled by the absorption of an electron from an upper level with the energy thus released appearing in the form of an Auger electron ejected from a nearby upper level. The Auger electrons are then detected in the electron energy analyzer[1], and measured values may be compared with published tables of atomic energy levels[2] to identify the particular impurity. Sensitivity for the technique is on the order of a hundredth of a monolayer coverage or about 10^{13} atoms per cm^2; detection depth is limited to several atomic layers.

The electron energy analyzer is of the spherical retarding field type.[1] This analyzer consists of three concentric, spherical grids fabricated from 100 mesh gold-plated tungsten cloth woven from one mil wire. These grids have approximately 90% transmission. Electrons are collected on a spherical screen coated with a fluorescent material which facilitates alignment of the electron beam. The primary beam is derived from a modified Superior Electronics 3k/5u electron gun arranged for glancing incidence.

III. APPLICABILITY OF AUGER SPECTROSCOPY TO SEMICONDUCTOR PROCESSING

To determine the applicability of Auger spectroscopy to the types of problems encountered in semiconductor device processing, it was decided that the first phase of this program would consist of an examination of a relatively small number of samples covering a number of specific process steps. The steps considered were wafer polishing, cleaning, first oxidation, base diffusion, emitter diffusion, masking and metalization. The results of this phase have been reported in the monthly progress letters and only selected data are presented below to indicate the usefulness of the technique.

The first samples examined were silicon wafers which had been cut, polished and cleaned by the supplier. These wafers were bright and showed no optical evidence of contamination, even though the wafers had not been subjected to the final cleaning just prior to first oxidation. An Auger spectrum obtained from one of these wafers is shown in Figure 3. The portion of the spectrum displayed exhibits a number of peaks corresponding to silicon, silicon oxide and carbon as labeled on the figure. Not shown is the structure at approximately 500 ev corresponding to oxygen which was seen on all samples. The main feature of interest on this sample is the structure in the spectrum lying between 100 and 200 ev. This spectrum has been shown to correspond to zirconium.

Discussions with the manufacturer suggested that this problem of zirconium contamination remaining on the in-coming wafers was of sufficient importance to warrant a more detailed investigation. It was learned that these wafers were polished using a commercial preparation supplied by the Tizon Chemical Corporation

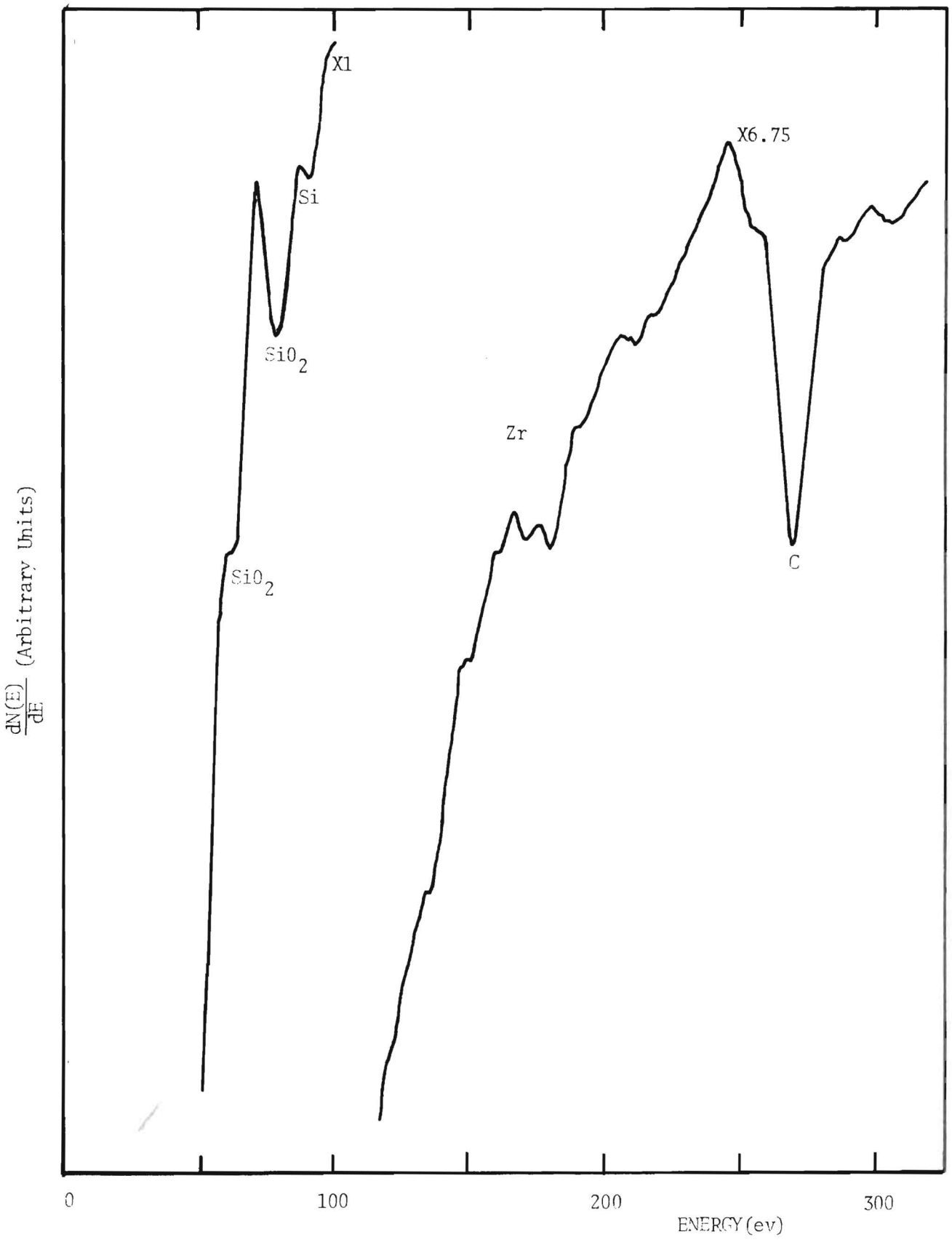

FIGURE 3. WAFER AFTER POLISHING (mild cleaning)

and designated as Lustrox 1000. The Tizon Corporation provided us with chemical samples and some information concerning composition. The major constituent indicated is ZrO (33%) with significant impurity concentrations of Na and Hf. Trace quantities of Al, Ca, Mg, Cu, Fe are also found, although no effort is made to routinely monitor concentrations. One proprietary ingredient is also present but was not specified.

To demonstrate that the observed impurity spectrum derived from zirconium residue left from the polishing operation comparison was made with published spectra for zirconium[4] and with spectra obtained from a silicon wafer intentionally contaminated with the polishing compound in question. The wafer was coated with small amounts of the Lustrox 1000 such that the thickness varied from heavy on one side of the wafer to zero coating on the opposite side. Spectra were then obtained at various points along this thickness gradient and a typical curve is shown in Figure 4.

Comparing the spectrum obtained from the intentionally contaminated wafer with that of the wafers as received (Figure 3) confirmed the conclusion that the incoming wafers were contaminated with a zirconium residue in spite of the clean optical appearance of these wafer surfaces. However, it was interesting to note that the amount of zirconium indicated by the Auger spectrum varied from wafer to wafer. This gives weight to the logical conclusion that the zirconium is present as essentially isolated particles of ZrO imbedded in the surface.

The next question of importance was that of removing this particular impurity before first oxidation. For comparison one of the polished wafers exhibiting significant zirconium contamination was removed from the Auger system and

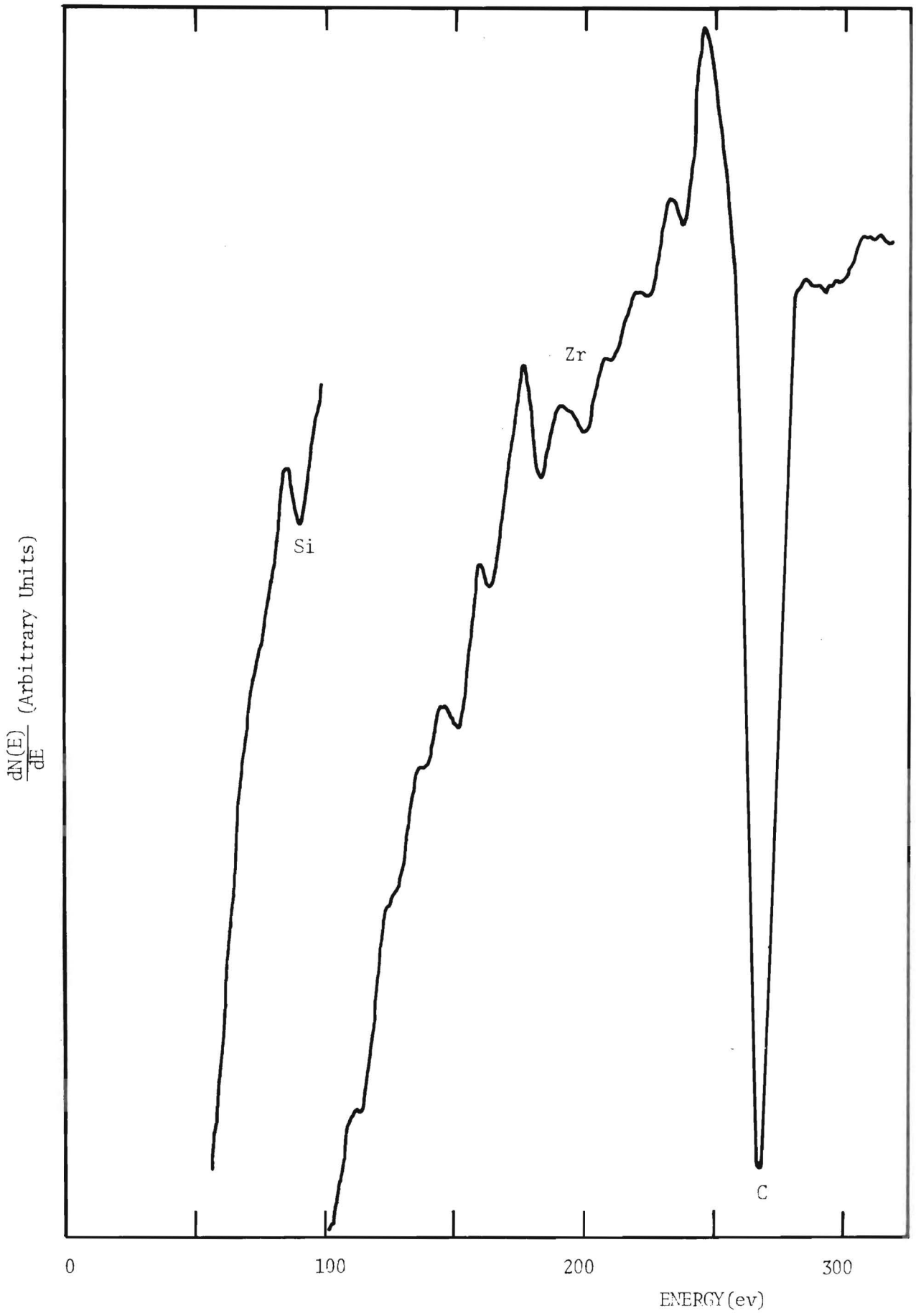

FIGURE 4. WAFER INTENTIONALLY CONTAMINATED WITH Zr

cleaned. This cleaning included a dilute HF dip and subsequent mild heating in vacuum. The resulting spectrum is shown in Figure 5. Again comparing this curve with that of Figure 3, it may be noted that the cleaning resulted in an enhancement of the carbon peak and a stripping of the silicon oxide as would be expected. This stripping action is evident in the Auger spectrum from the disappearance of the silicon oxide peaks and the increase of the pure silicon Auger peak. On the other hand, the Auger peaks corresponding to the zirconium were little changed and were even increased in intensity, probably due to the removal of other superficial impurities.

To round out this question of zirconium removal, other measurements were made on several wafers supplied after the final cleaning just prior to first oxidation. These wafers showed considerable improvement with regard to zirconium contamination, although there was evidence, as indicated in Figure 6, to show that the removal of the impurity was not complete. This fact was substantiated in measurements on samples considered in the second phase of the program and discussed in the next section.

The next process step considered in this study was first oxidation. A typical curve for the two wafers examined is shown in Figure 7. The samples at this particular processing step appeared to be very clean. Carbon contamination was reduced, and, as would be expected, the pure silicon peak disappeared leaving a large silicon oxide peak as shown in the figure. On one of these samples there was a slight indication of impurity structure in the region around 200 ev. This structure was tentatively identified as ruthenium, and it was suggested that the source might be in connection with the quartz tubes used in the oxidation furnace. It must, however, be noted that the data available was insufficient for a firm con-

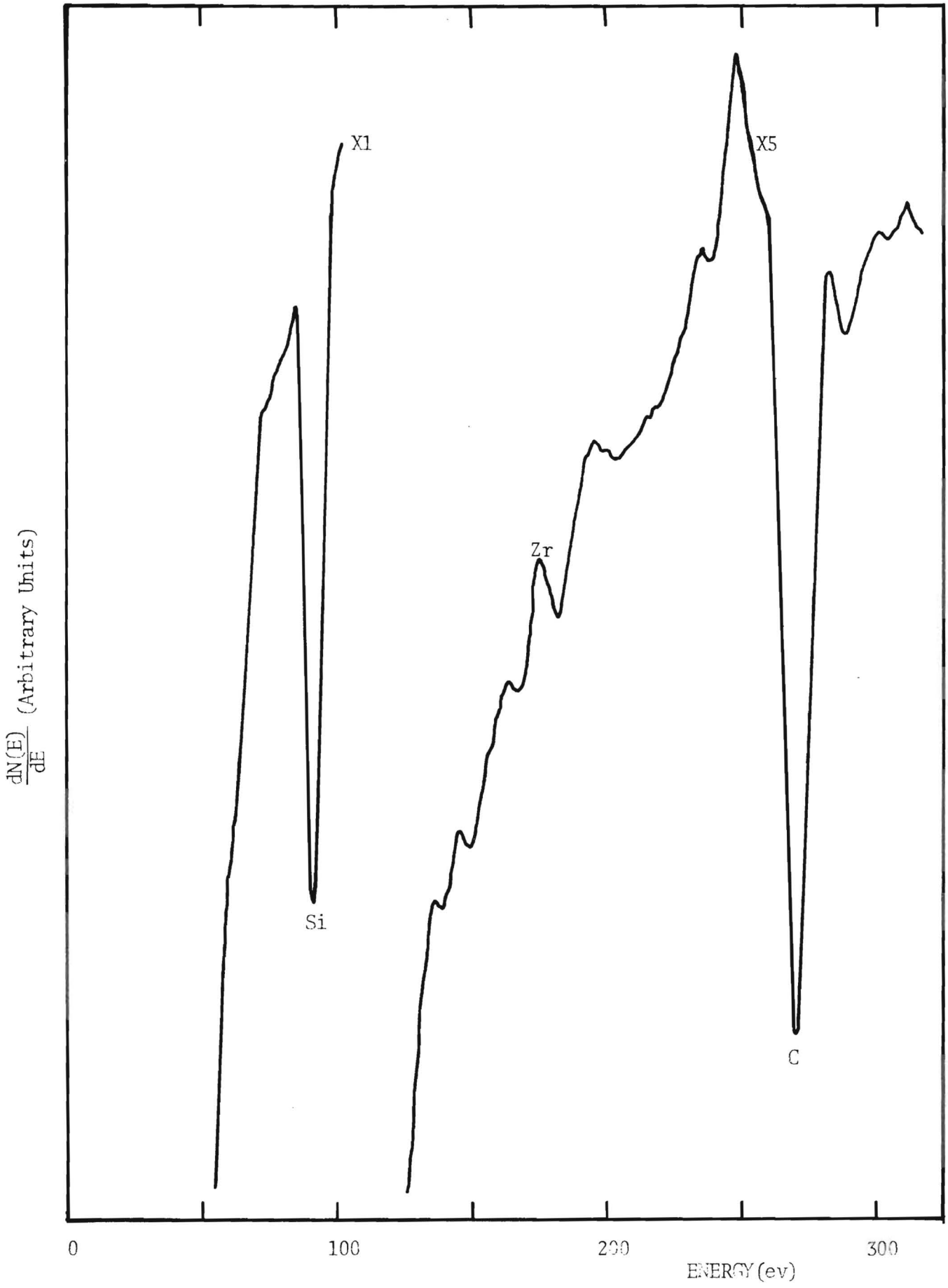

FIGURE 5. WAFER AFTER HF DIP AND HEATING

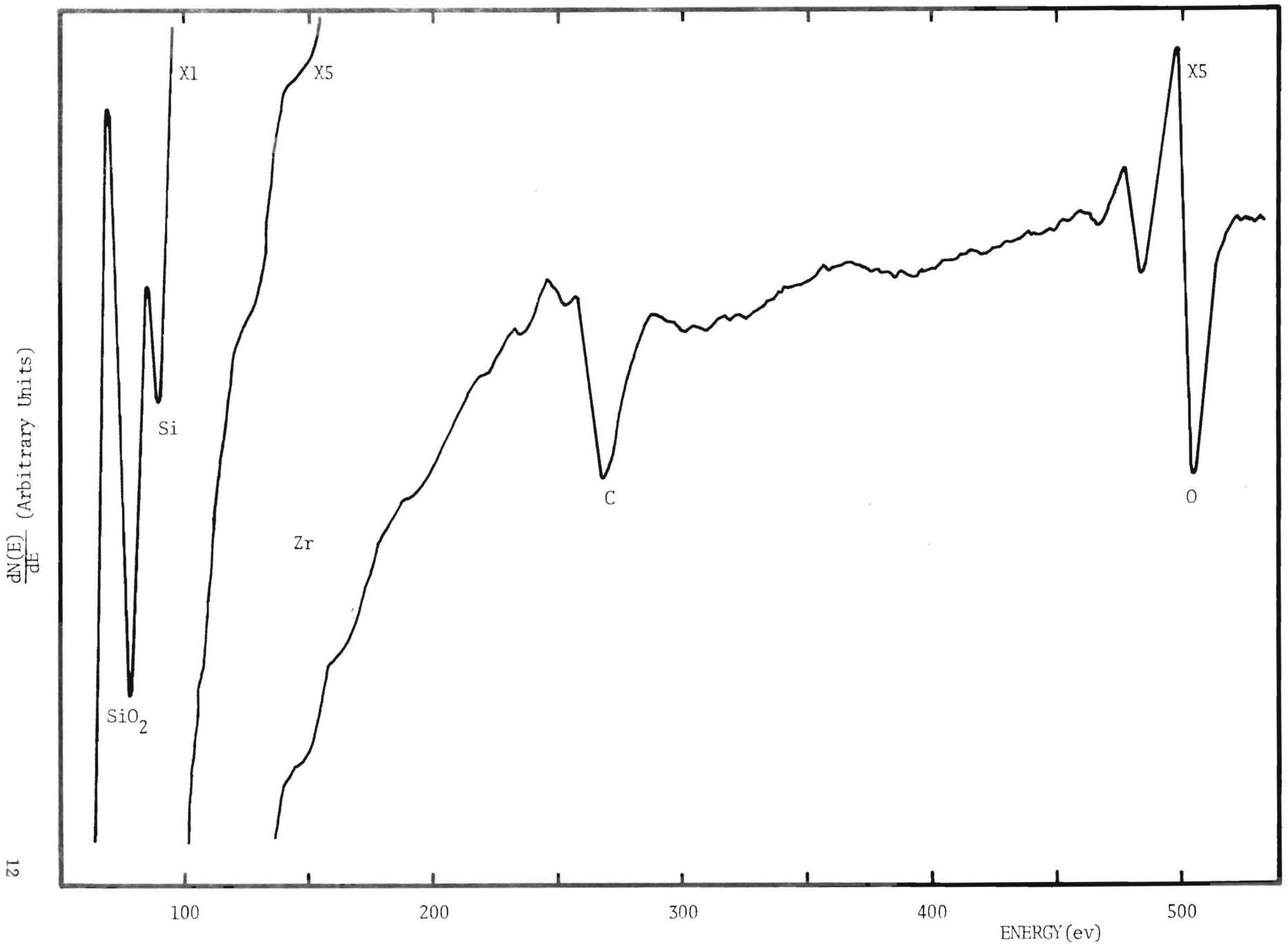

FIGURE 6. WAFER CLEANED FOR FIRST OXIDATION

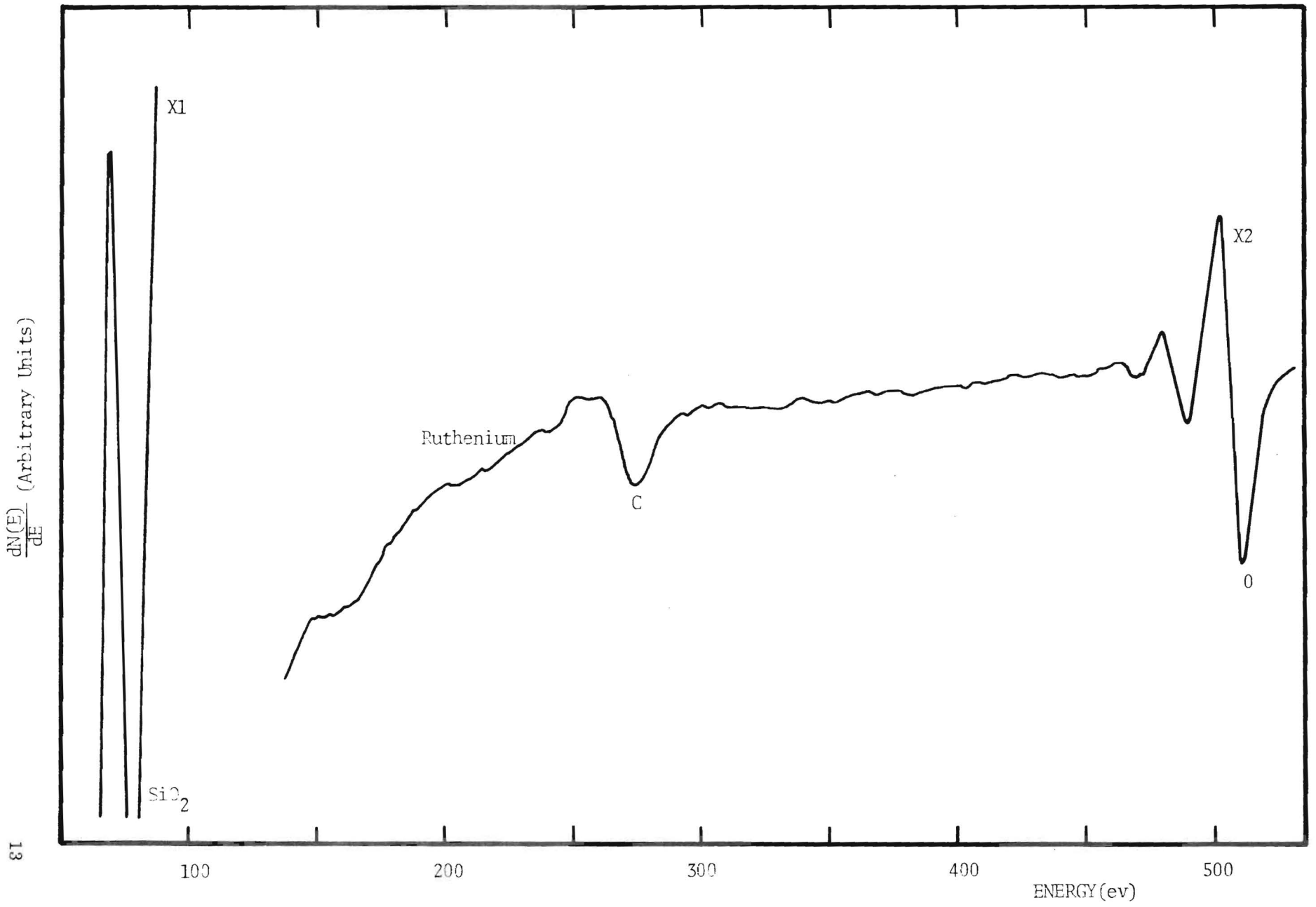

FIGURE 7. WAFER AFTER FIRST OXIDATION

clusion to be drawn.

Figure 8 shows a curve obtained after final base diffusion. There is little difference between this curve and the curves obtained after the first oxidation. It may again be noted that slight structure corresponding to the zirconium spectrum was observed. No evidence for boron was found probably because at this point the surface boron glass had been etched off and the bulk diffused levels were below the detection sensitivity for the instrument.

Similar curves were obtained after final emitter diffusion. Typical of these curves is the Auger spectrum of Figure 9. The only essential difference in this and the previous curve is the presence of the phosphorous peak corresponding to the layer of this impurity left on the surface after this step in the process.

The remaining samples analyzed were concerned with contact masking and the aluminum evaporation. Figure 10 is representative of curves obtained on two samples after contact mask, aluminum evaporated on and etched off. This Auger distribution brings out features similar to the earlier curves, except for the Al contribution to the peak intensity near 60 ev and, more significantly, strong impurity peaks representing potassium and chromium. These impurities, indicated in the figure, were not uniformly distributed on the wafer surface; some points on the wafer were found showing little of this contamination while others were heavily contaminated.

Similar curves were obtained after contact mask, sample cleaned and ready for aluminum evaporation. This situation is illustrated in Figure 11.

The final two curves show results obtained for the wafer after the aluminum mask. Figure 12 shows that the spectrum is dominated with carbon and oxygen, while Figure 13 obtained on a different spot shows heavy chromium contaimination.

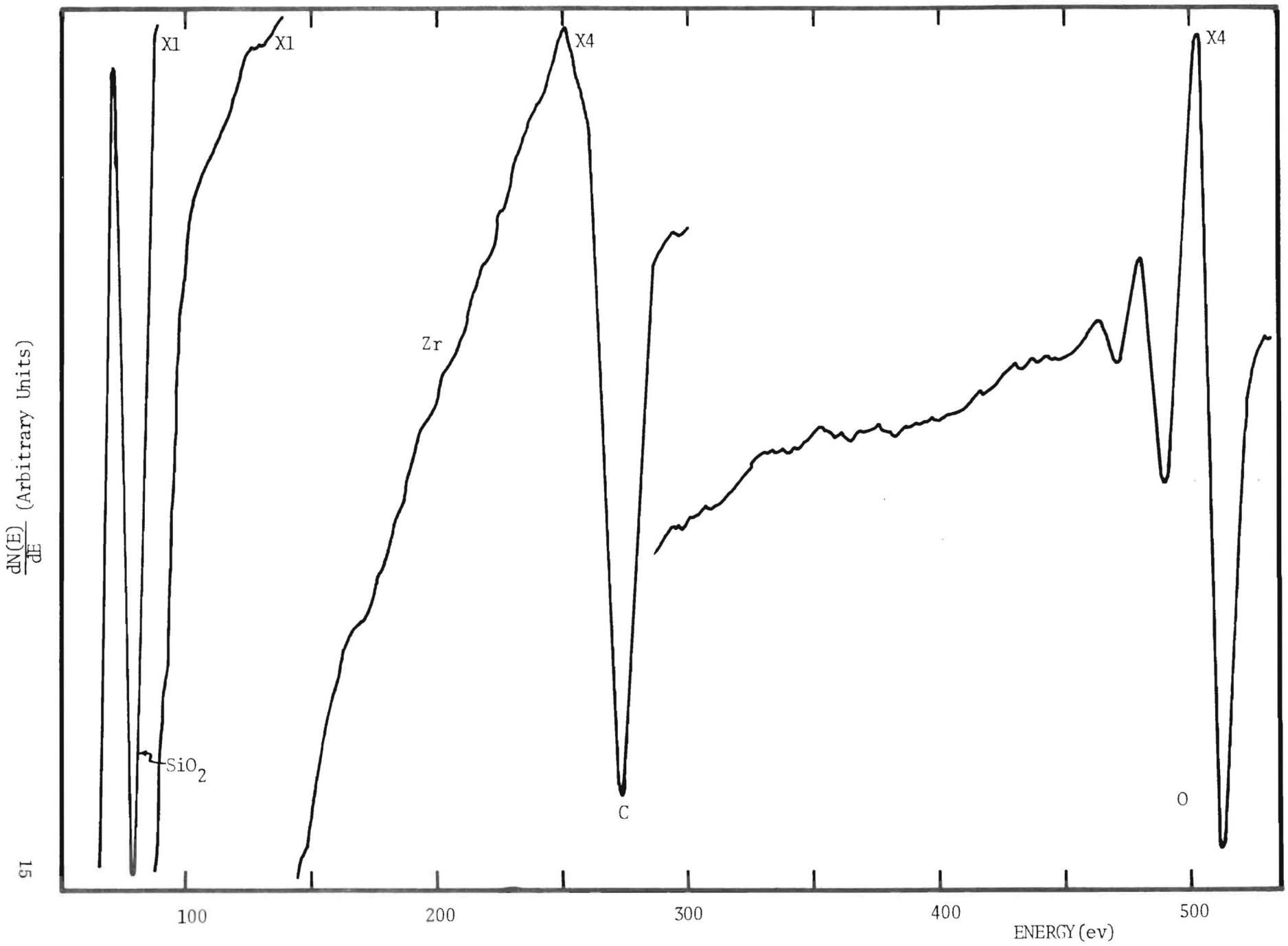

FIGURE 8. WAFER AFTER BASE BORON DEPOSITION

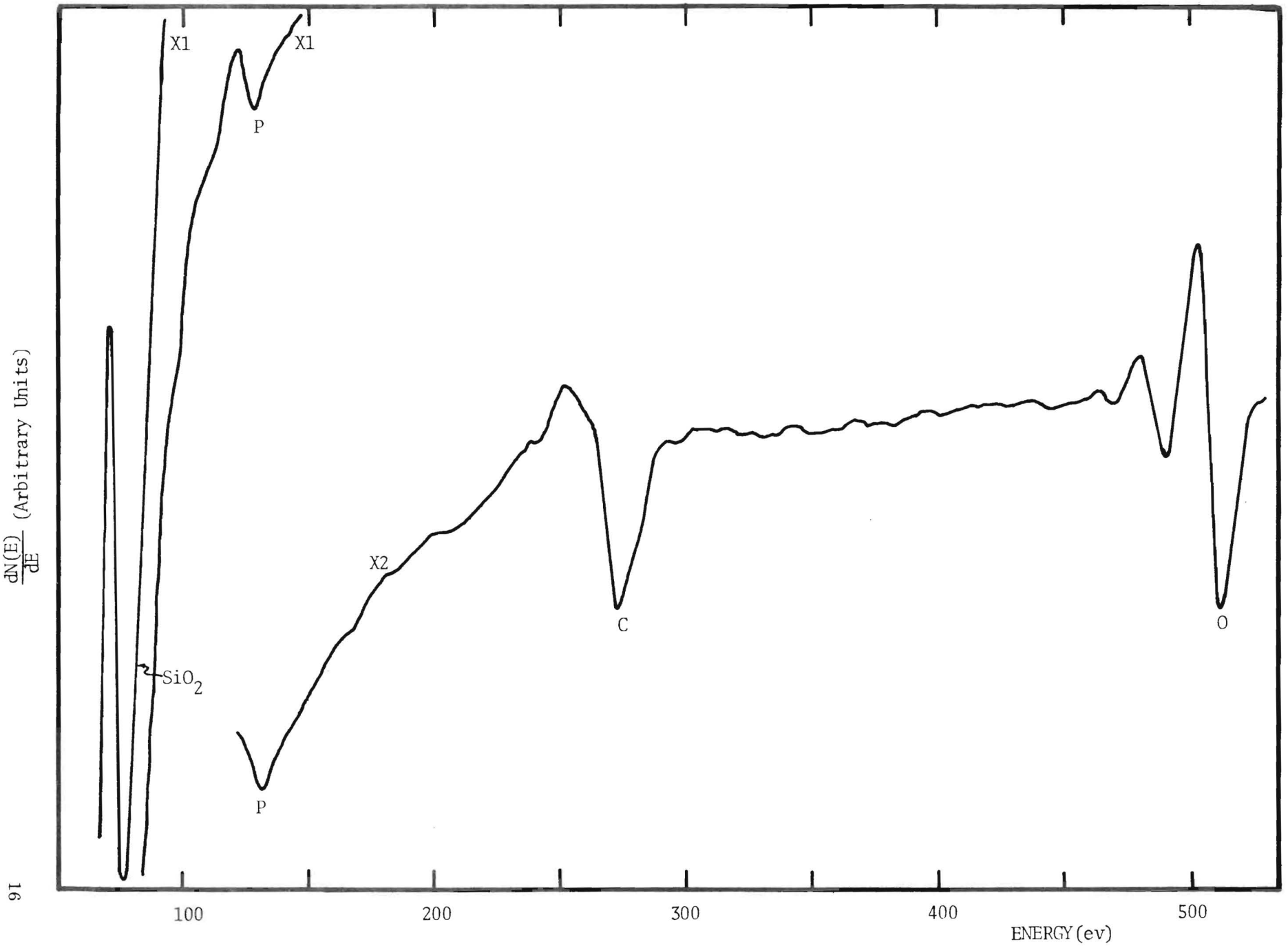

FIGURE 9. WAFER AFTER FINAL EMITTER DIFFUSION

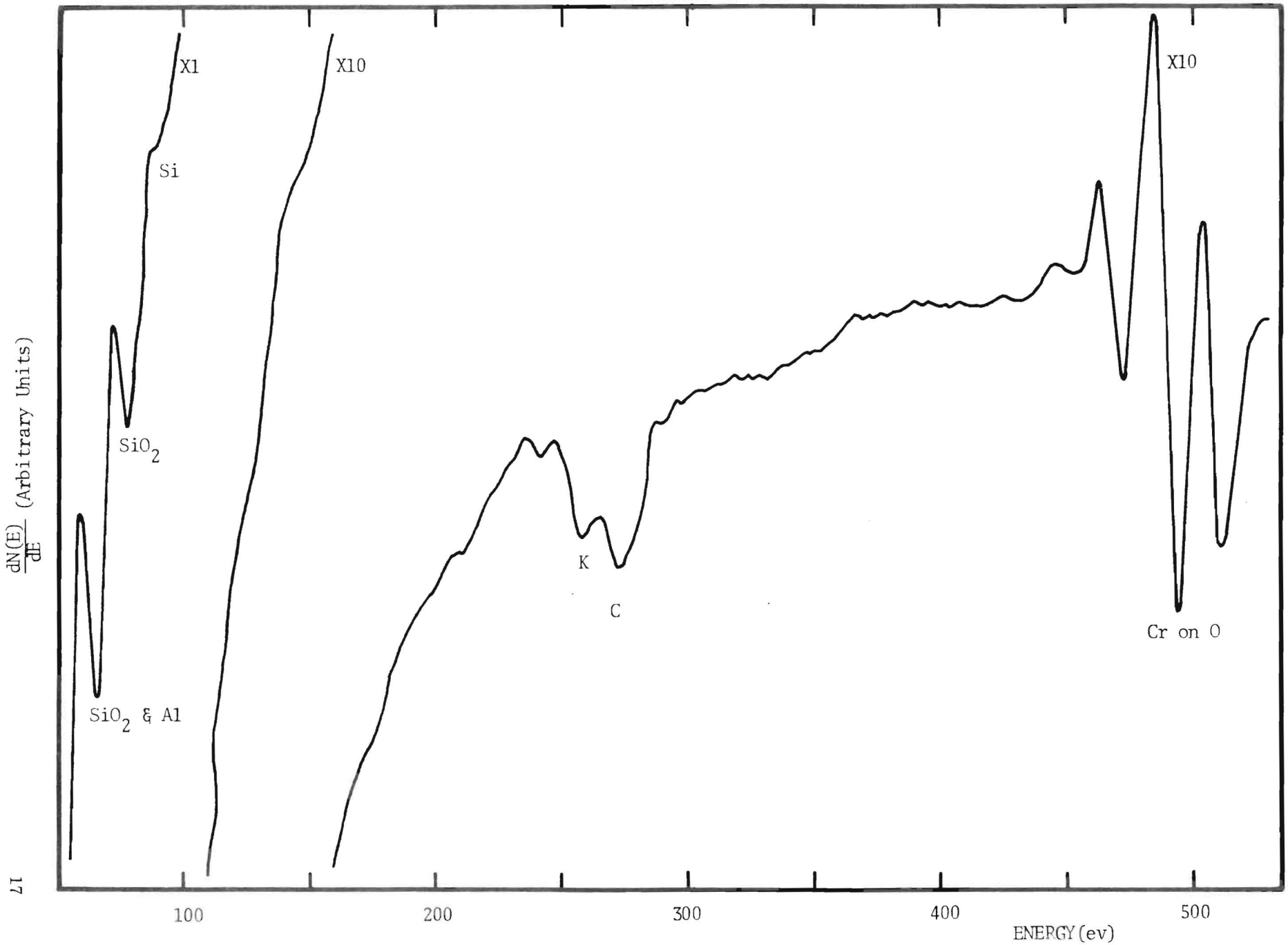

FIGURE 10. WAFER AFTER CONTACT MASK; Al EVAPORATED ON AND ETCHED OFF

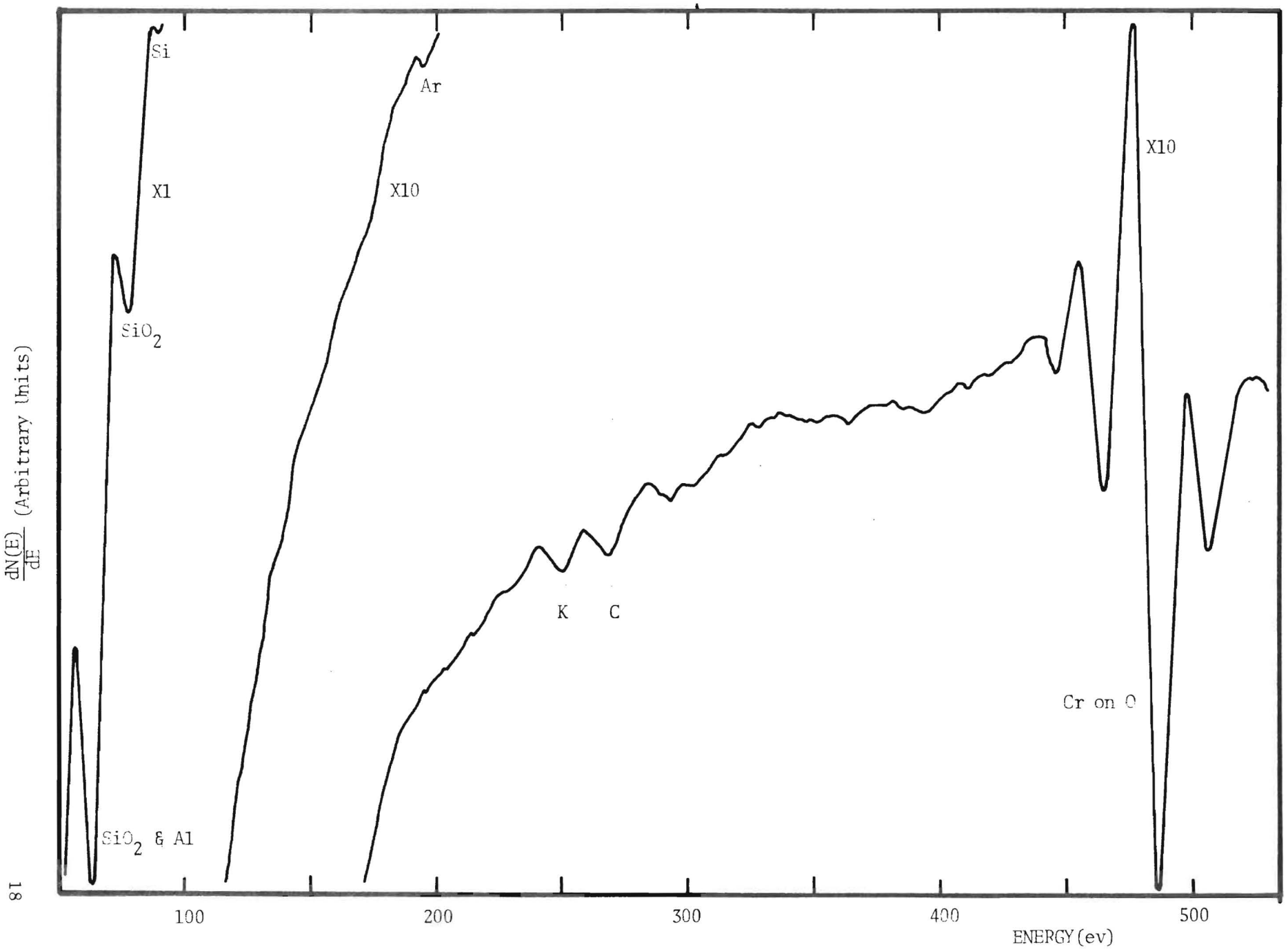

FIGURE 11. WAFER AFTER CONTACT MASK; CLEANED AND READY FOR Al EVAPORATION

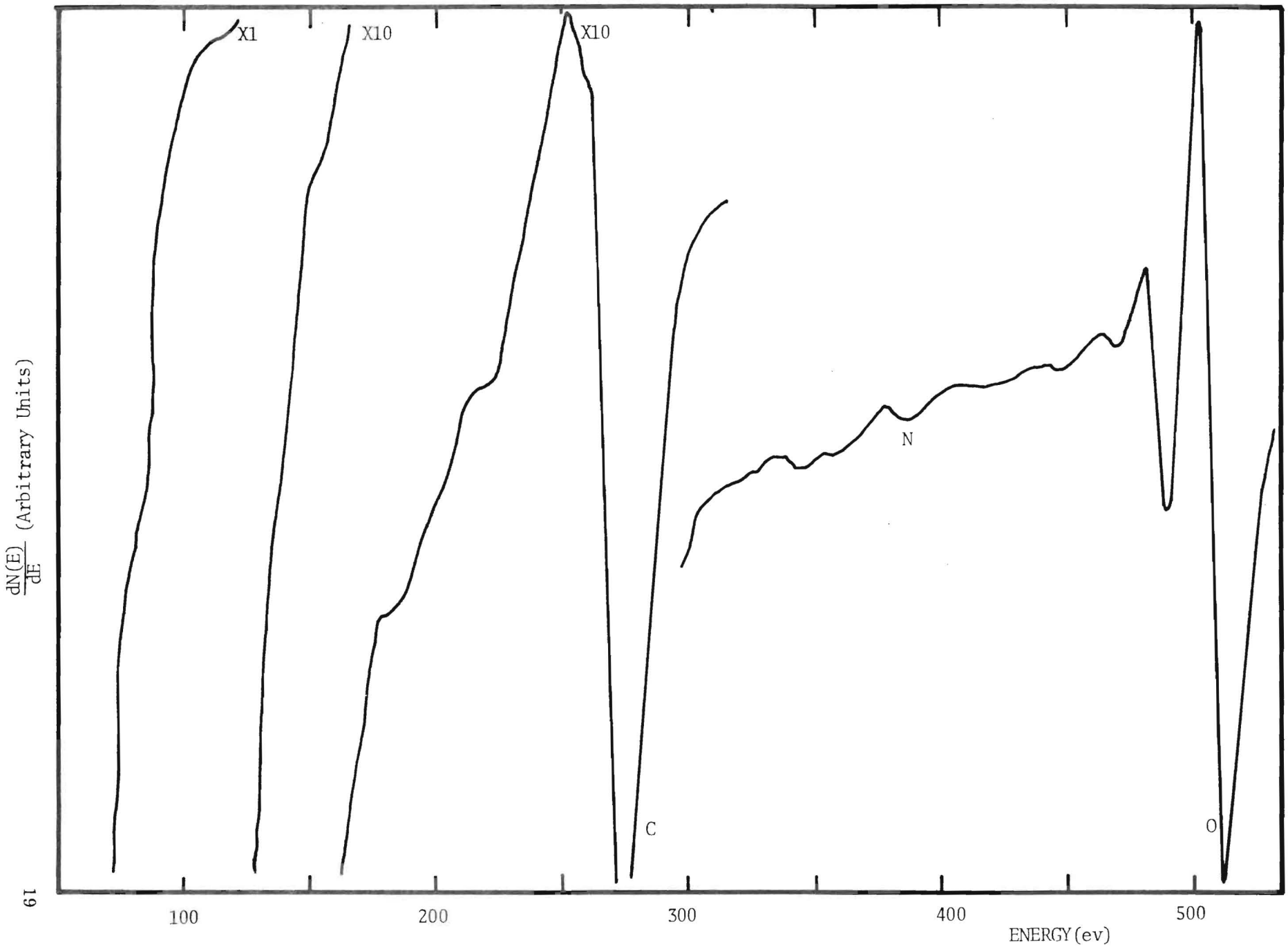

FIGURE 12. WAFER AFTER A1 MASK

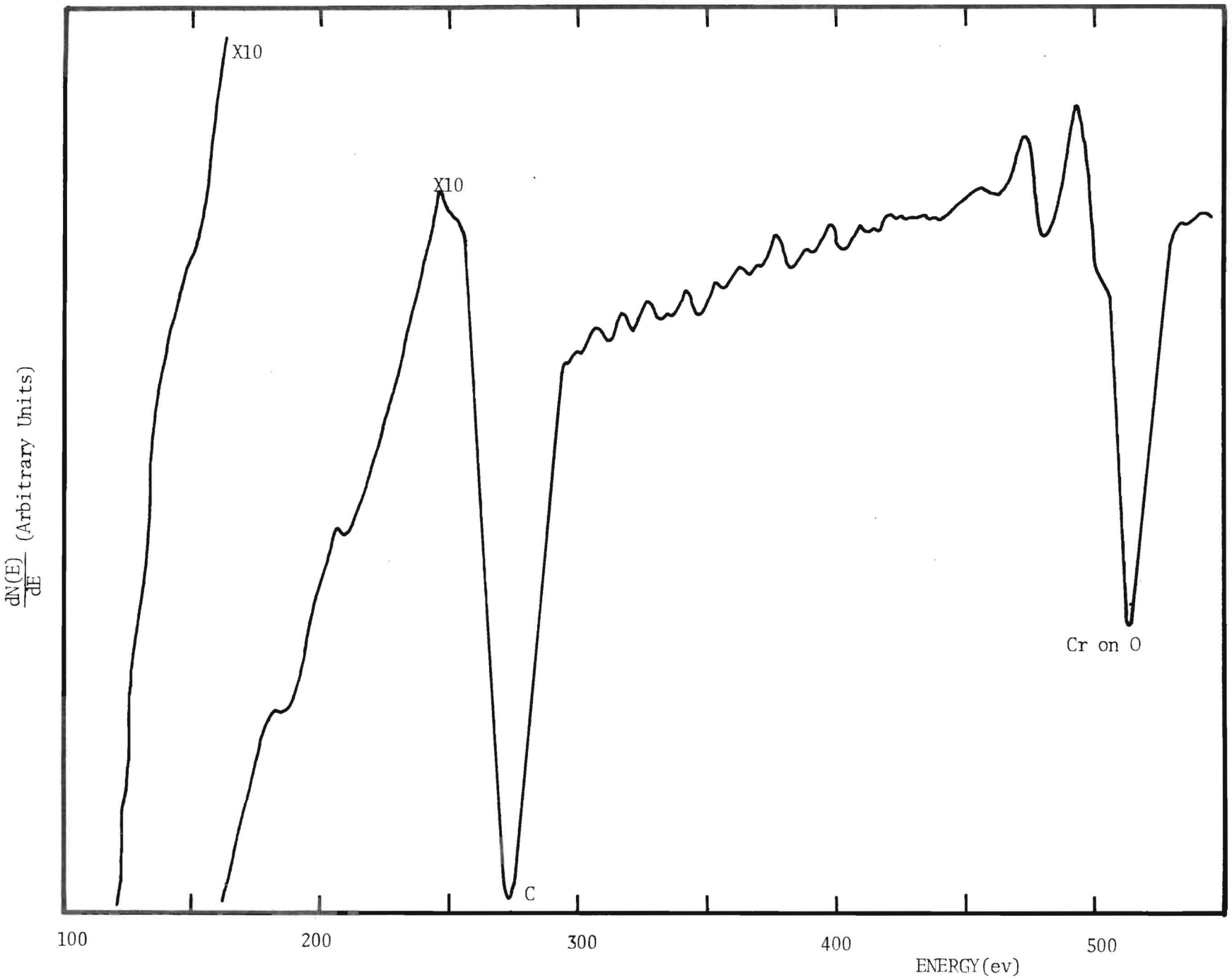

FIGURE 13. WAFER AFTER A1 MASK

The sources of these impurities were not specifically identified although a localized nature was implied.

All total, in the first phase of this study of the applicability of Auger spectroscopy to semiconductor processing, thirty wafers were examined for impurities including six supplied by NASA. The results obtained and summarized in this section clearly show that there are contamination problems inherent in the types of processing used to manufacture semiconductor devices which can be studied and monitored using this electron scattering technique. Results of this first phase have been discussed with the manufacturer supplying these wafers and, already steps have been taken to upgrade the processing methods to reduce residual contamination. These improved process methods are further discussed in the final section of this report.

IV. EXTENDED EVALUATION OF SELECTED PROCESS STEPS

After demonstrating that Auger Spectroscopy could be successfully applied to contamination problems of interest in semiconductor processing, the next phase of the program was designed to provide a more detailed examination of selected process steps. This would more completely specify the extent of observed contamination states and lay the groundwork for correlations with variations of electrical parameters. Results obtained in examining these process steps are presented below.

A. After First Oxidation

At this step ten wafers were examined as received following first oxidation. These wafers represented two each selected from five batches. Contaminants observed included zirconium, ruthenium, sulfur and a peak corresponding to either boron or chlorine. The curve presented in Figure 14 is typical of curves obtained on the majority of the ten wafers. For each wafer at least five Auger spectra were obtained at different positions on the wafer surface.

The most outstanding features seen in the Auger distribution of Figure 14 are the peaks corresponding to silicon oxide and oxygen as indicated on the curve. However, of more interest are the peaks representing ruthenium and zirconium. These impurities were observed on all of the ten wafers examined with relatively little variation in amounts of the indicated impurities. By comparison with the major peaks found in the spectrum one would estimate the average surface coverage to be substantially below a full monolayer. To verify the ruthenium structure comparison was made with published spectra[4] for ruthenium foil. The zirconium spectra was verified by comparison with measurements described earlier.

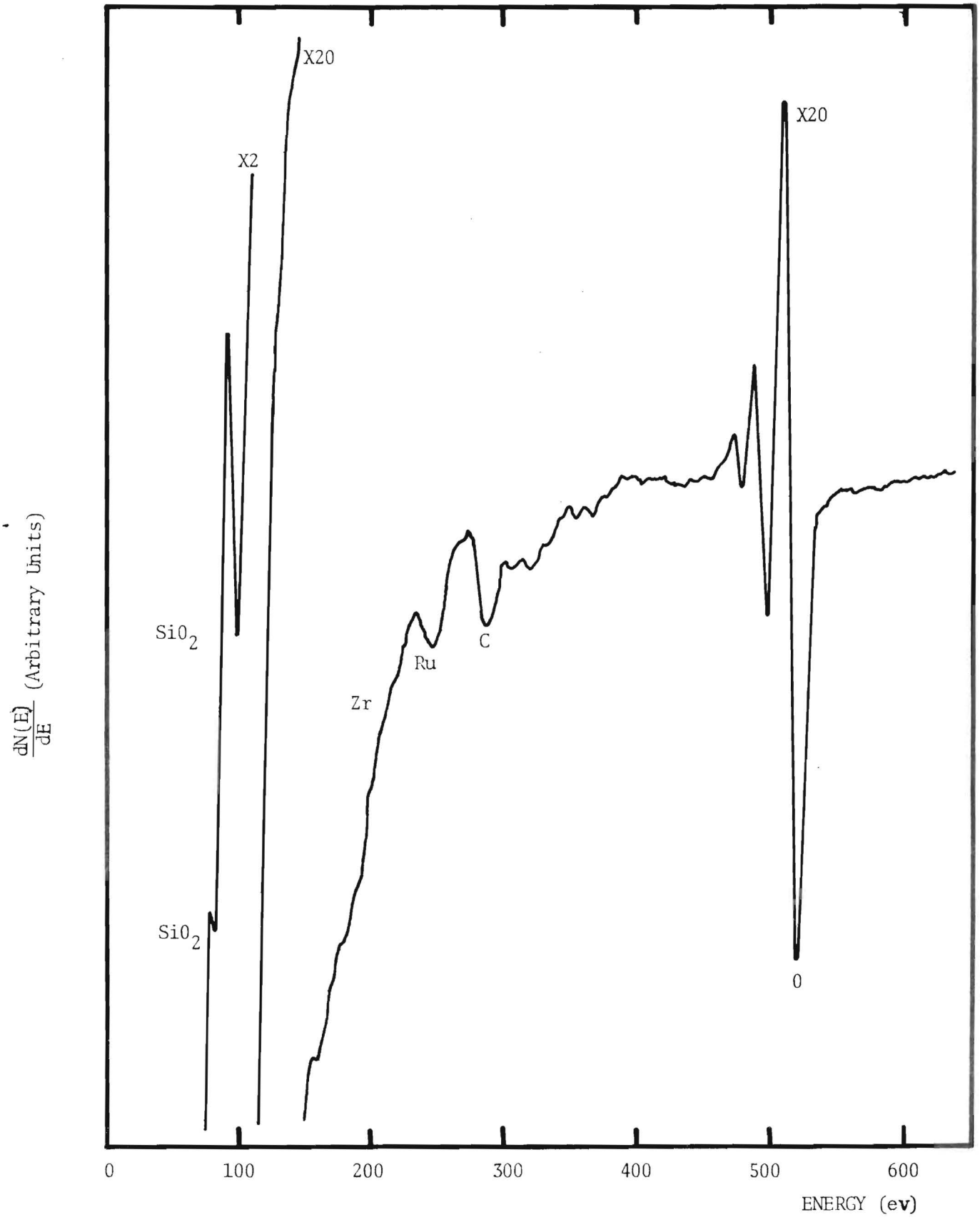

FIGURE 14. TYPICAL SPECTRUM OF WAFER AFTER FIRST OXIDATION

In addition to these impurities sulfur was found to be a minor impurity on all the wafers after first oxidation, although, in this case, the amount present varied to a greater extent. Figure 15 shows strong sulfur contamination which was observed on two wafers. This curve also shows ruthenium structure even though the zirconium spectrum is below detectable limits.

In the case of two wafers a strong peak was also observed at 180 ev which could be either boron or chlorine. This is shown in Figure 16. It must be recalled that the Auger peak alone is not sufficient information to differentiate between the possible contaminants of chlorine and boron. One of these wafers was one which also exhibited greater sulfur contamination than generally found.

B. After Photoresist Removal

The second step examined in greater detail was the removal of photoresist following base masking. Ten wafers were examined and generally found to be rather clean, as indicated in the curve of Figure 17. This curve shows the normal silicon oxide peaks and carbon as well as minor impurity concentrations of sulfur and silver. It was the latter impurity, silver, which proved to be of greatest interest as discussed in the next section. Silver was found in sub-monolayer quantities on several of the ten wafers.

This particular process step was difficult to characterize with Auger data because of surface charging. This charging resulted in peak splitting for some of the Auger curves obtained--its cause was not determined. In spite of this problem, some good data was obtained on each of the ten wafers.

C. After Base Boron Diffusion

Again at this step ten wafers were examined and electrical measurements

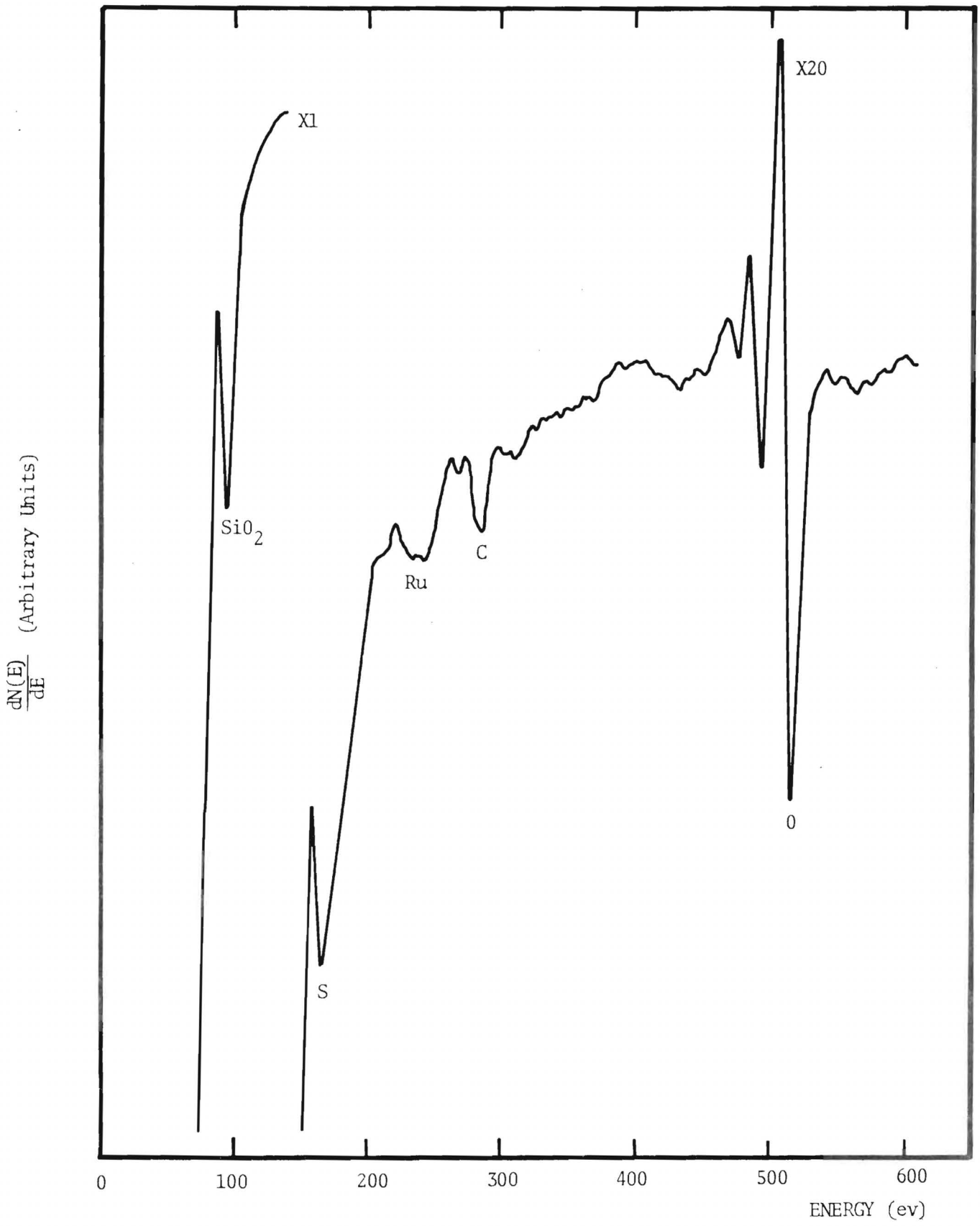

FIGURE 15. WAFER AFTER FIRST OXIDATION SHOWING S CONTAMINATION

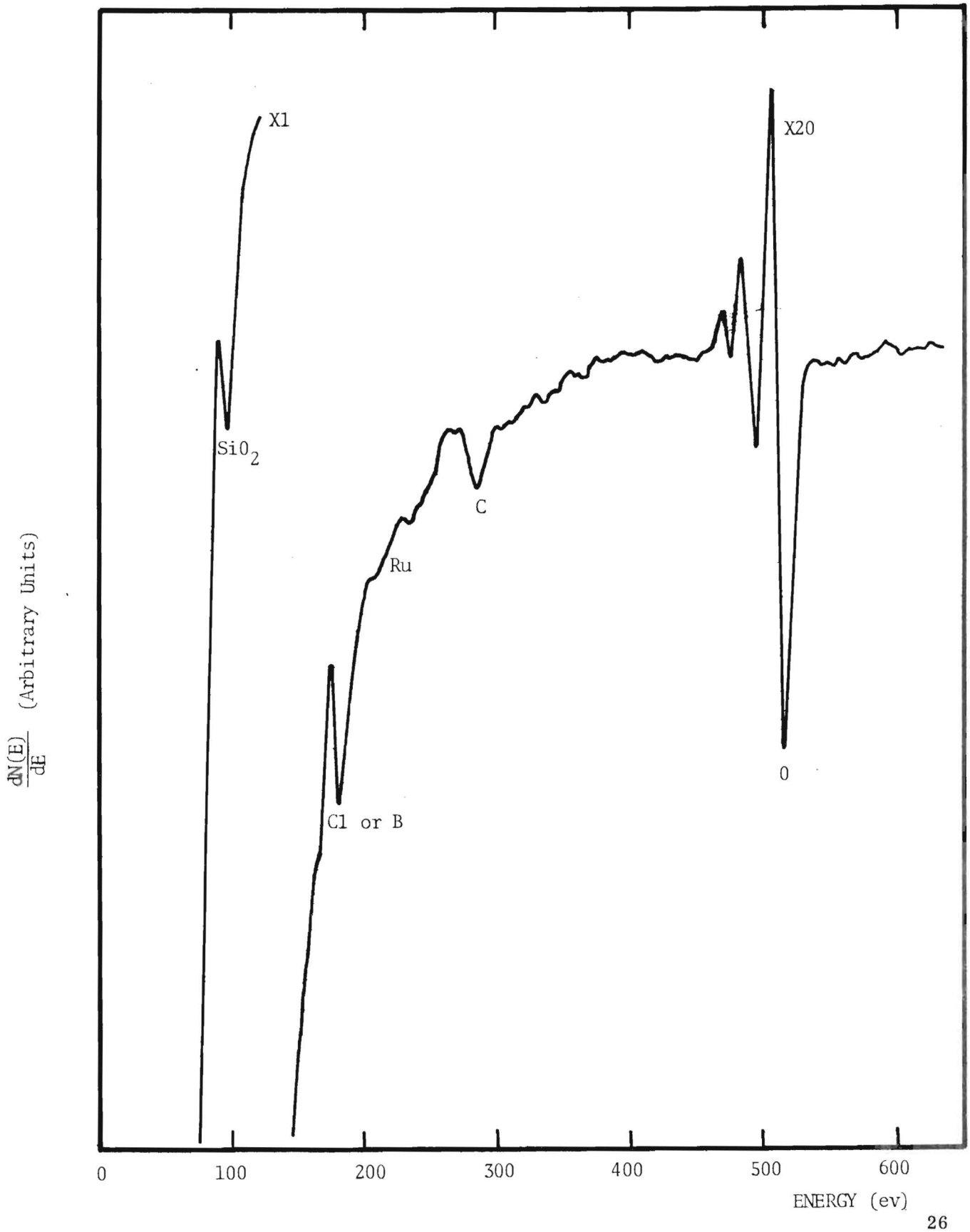

FIGURE 16. WAFER AFTER FIRST OXIDATION SHOWING Cl or B CONTAMINATION

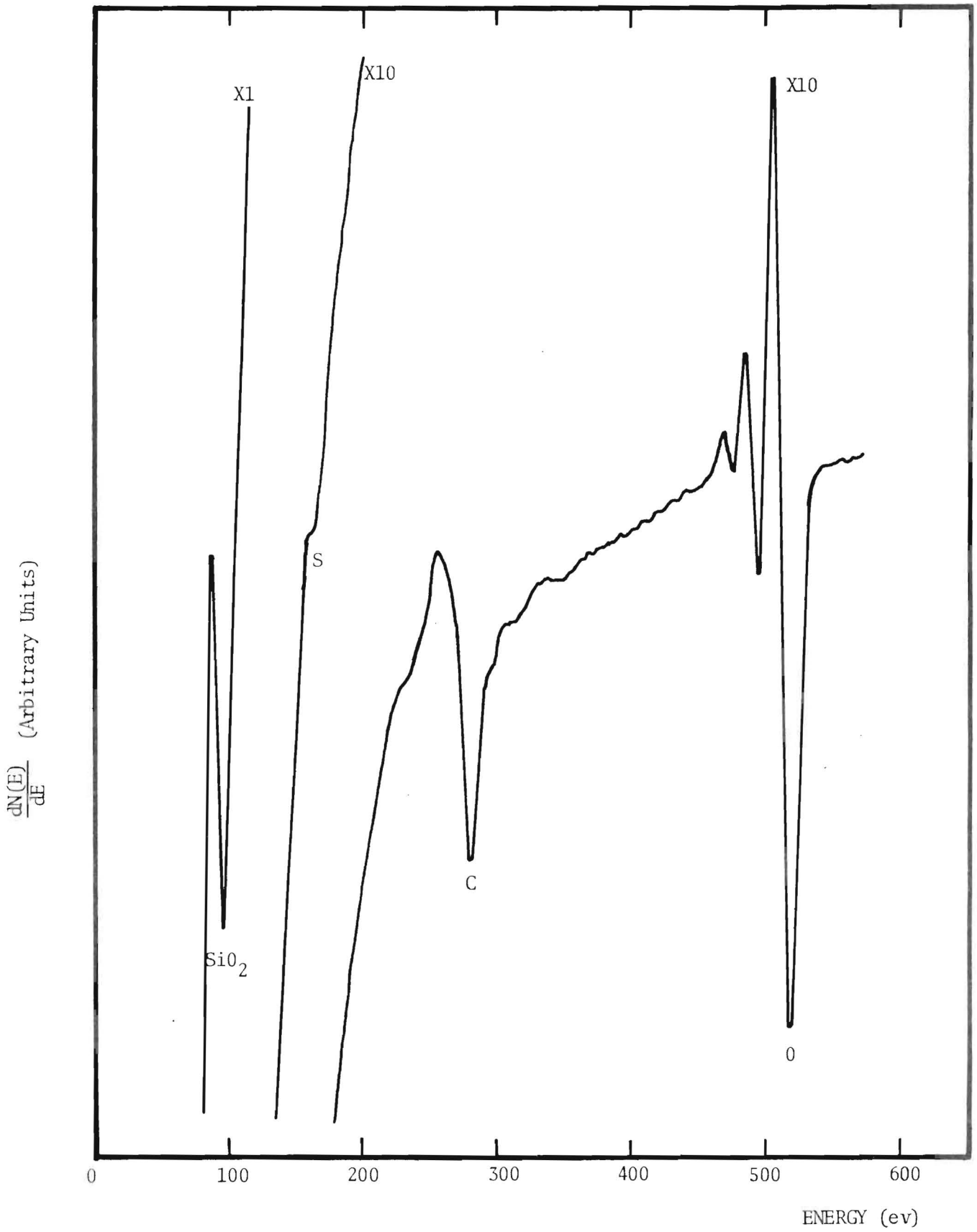

FIGURE 17. TYPICAL WAFER AFTER BASE MASK, PHOTORESIST REMOVED

were added to the Auger spectra in an effort to establish a correlation between surface impurities and collector-base diode leakage. Interestingly, these wafers were among the cleanest of all wafers examined. However, minor impurities were observed including carbon, ruthenium, and another impurity of particular interest, silver.

The Auger spectrum of Figure 18 is typical of the majority of the spectra obtained after base diffusion. This curve shows large silicon oxide and oxygen peaks as expected and a moderate sized carbon peak which is not especially significant compared with other samples characterized. Of note is the fact that the boron peak is very small even when large amounts of surface boron might be expected; a plausible explanation for this observation is surface masking.

On one wafer the surface boron was slightly enhanced as may be seen in Figure 19. Ruthenium was observable though not significant on five out of the ten wafers. This is illustrated in Figure 20.

The impurity of greatest interest is that identified as silver and shown in Figure 21. This impurity was observed in fractional monolayer quantities on several wafers and is of interest because the wafers exhibiting this impurity seemed to have the lowest values of diode leakage.

To establish this correlation, diode leakage currents were measured for a number of diodes on each of the ten wafers. These current measurements were made in subdued lighting with ten volts applied reverse bias. Average leakage was approximately 0.35 microamps although some diodes showed leakage currents as high as 1.9 μA and others as low as 0.03 μA. Generally the values of diode leakage measured were reasonably consistent over any particular wafer. The wafers

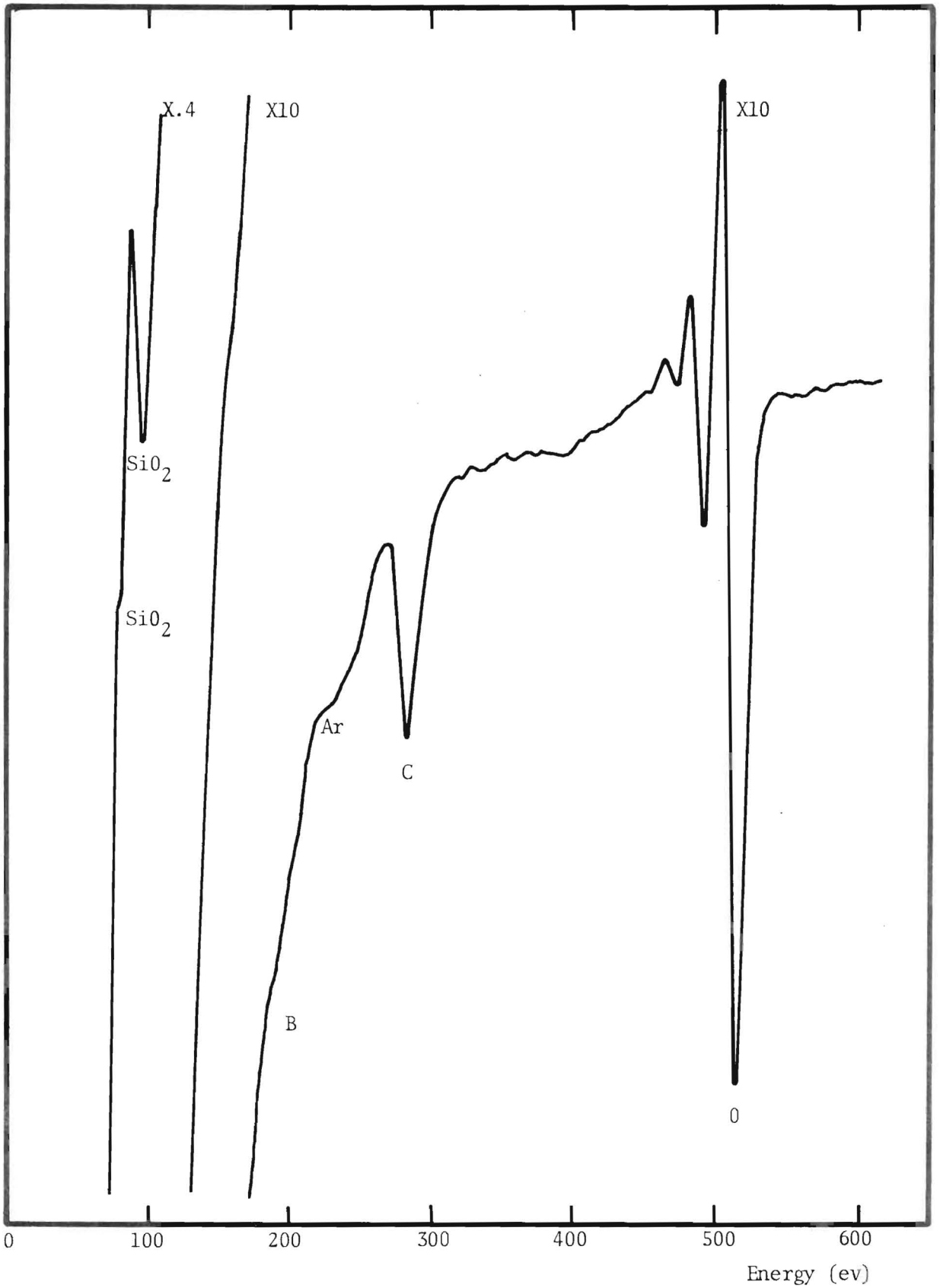

FIGURE 18. TYPICAL WAFER AFTER BASE DIFFUSION

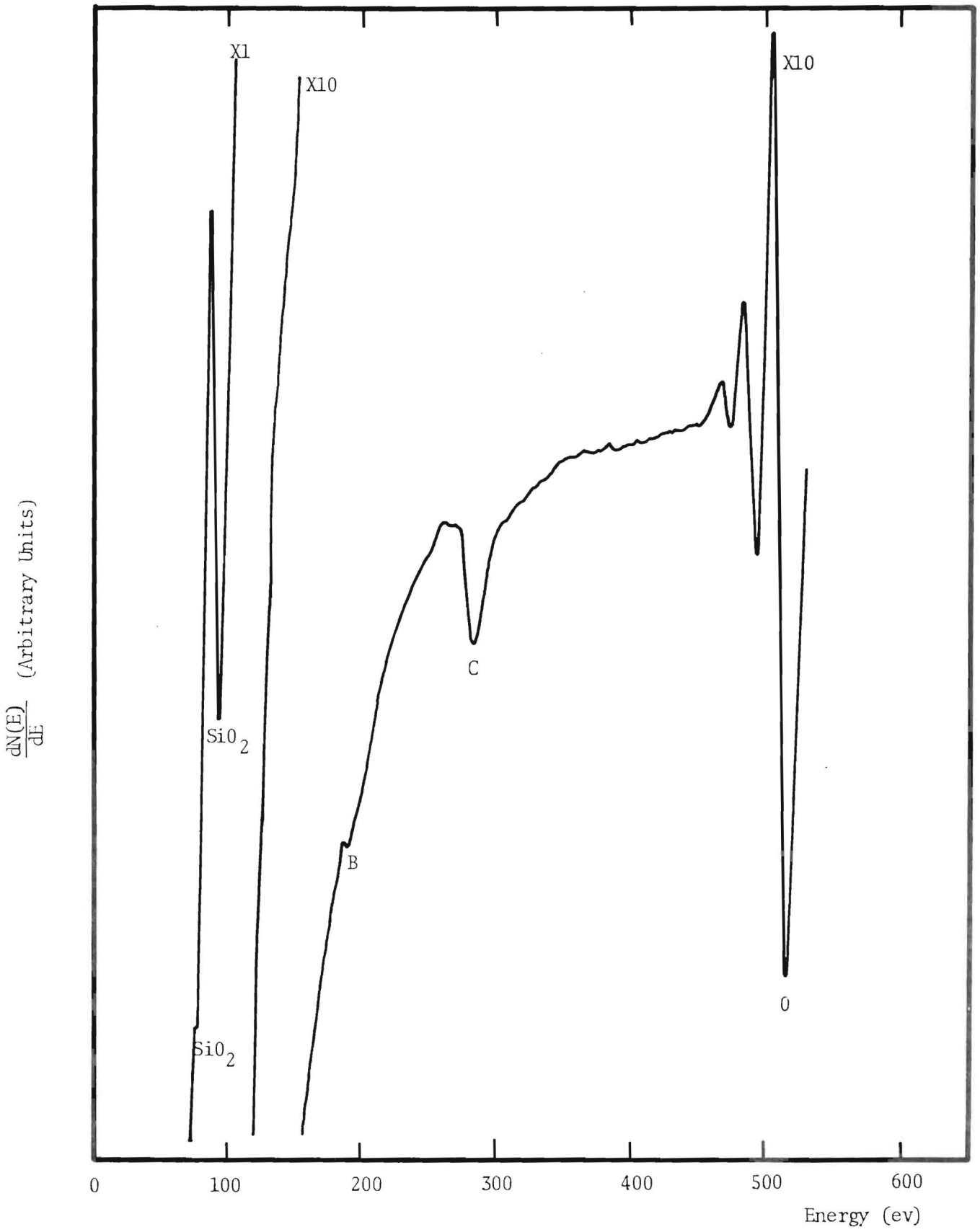

FIGURE 19. WAFER AFTER BASE DIFFUSION SHOWING SURFACE BORON

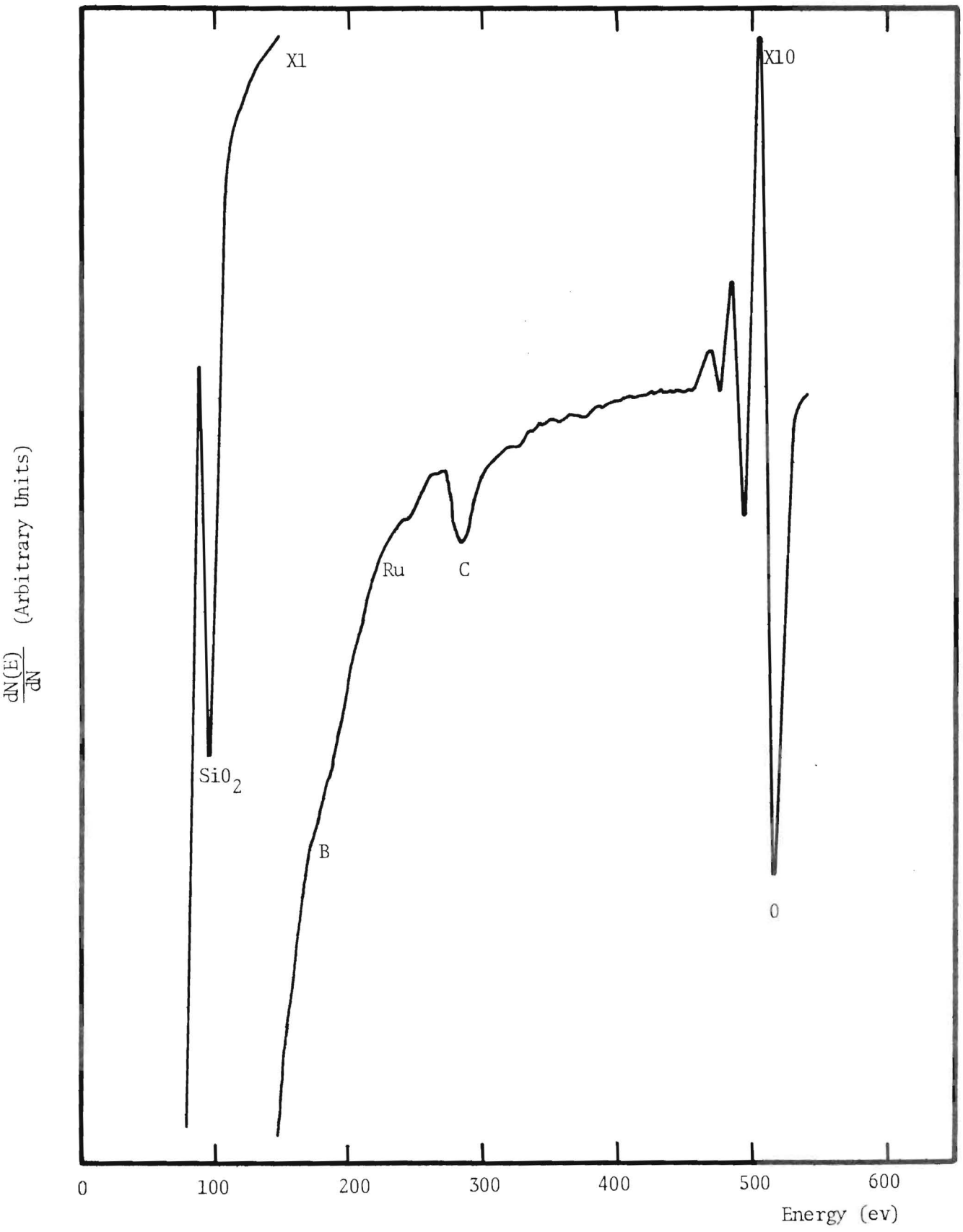

FIGURE 20. WAFER AFTER BASE DIFFUSION SHOWING Ru

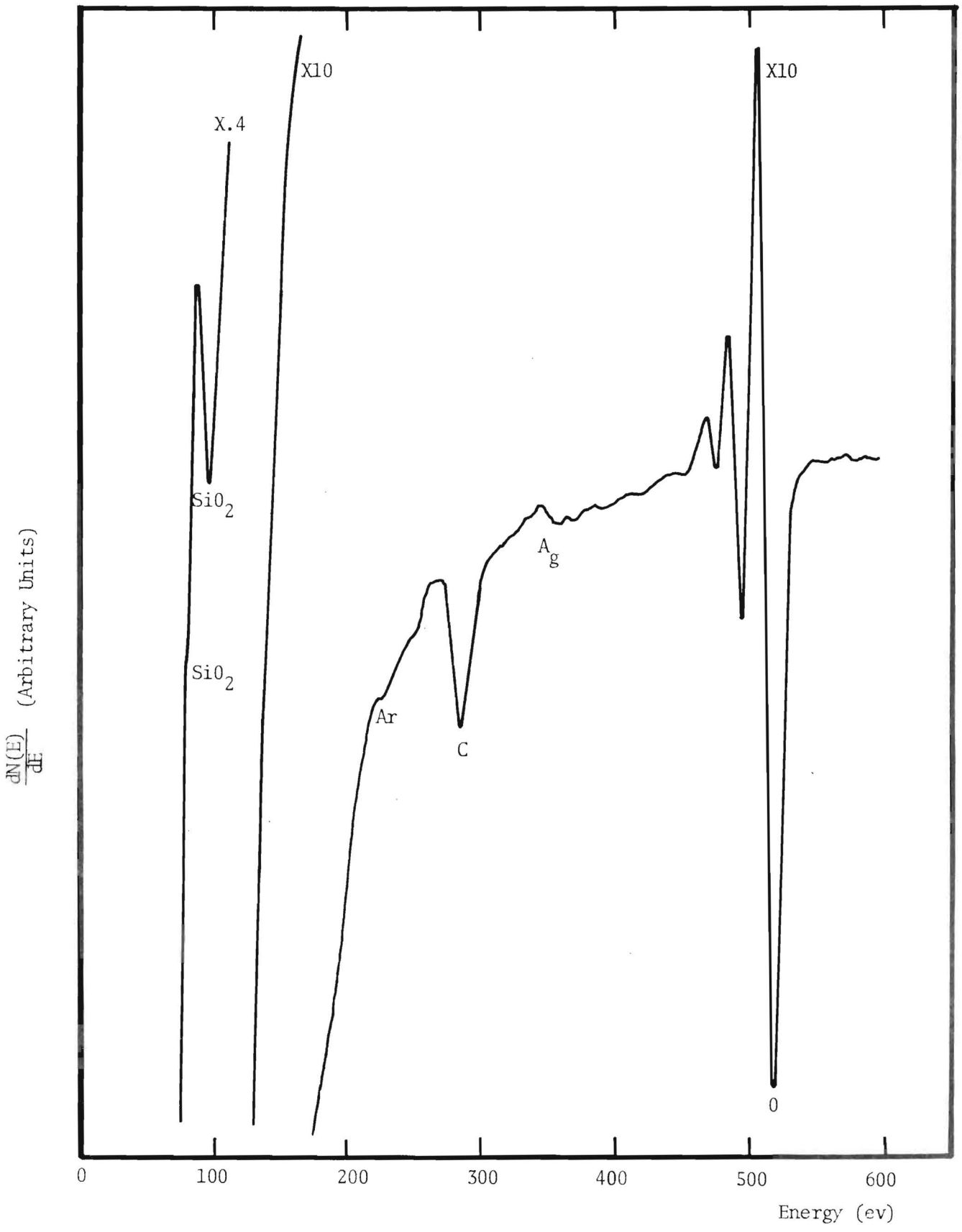

FIGURE 21. WAFER AFTER BASE DIFFUSION SHOWING A_g CONTAMINATION

measured fell generally into two classes with diode leakages above and below approximately 0.25 μA. Comparisons were made within batches simultaneously loaded into the five sample turret for sequential Auger analysis.

In the first five sample batch average values of diode leakage were found to be 0.19, 0.13, 0.28, 0.24 and 0.13 microamps for the five wafers respectively. Comparing these figures with the Auger data it was observed that both of the wafers with the lowest leakage values exhibited surface contamination of silver. However, the intensity of the silver peak for one of these wafers was somewhat smaller than shown in Figure 21. No silver was seen in curves obtained for the other three samples in this batch.

Four of the five samples in the second batch had average leakage values of 0.60, 0.28, 0.79 and 0.67 microamps. The fifth wafer was inadvertently damaged in handling and so data obtained on this wafer are not included. It may be noted that the lowest value of average leakage for this batch is higher than measured for the first batch. However, there is still a significant difference between the value of 0.28 μA and the other values measured. In examining the corresponding Auger data, it was again found that the wafer with the lower leakage exhibited significant surface contamination of silver. No silver was observed on the other three wafers.

The source of silver contamination or its role in affecting the diode leakage currents at this stage of device fabrication are at this point unclear. It appears that the silver may be a residue associated with the photoresist operation or its removal. The mechanism involved in the affect on the values of leakage would require more extensive investigation to obtain a clearer understanding of this problem.

D. After Emitter Diffusion

The ten wafers examined after emitter diffusion exhibited a broader range of low-level contamination than previously observed at other steps. Contaminants included phosphorous, carbon, ruthenium, silver, calcium and oxygen. As for the previous step electrical measurements were made along with Auger spectra determinations in an effort to establish a correlation between break-down voltages and surface contamination.

An Auger curve typical of the wafers after emitter diffusion is shown in Figure 22. This spectrum shows, in addition to carbon, oxygen and silicon oxide, minor contamination of phosphorous and nitrogen. It was further observed that the level of carbon contamination varied significantly from point to point on the same wafer and from wafer to wafer. Furthermore, four of the ten wafers exhibited ruthenium as indicated in the Auger curve of Figure 23. Significantly three wafers also gave evidence of silver as a surface impurity as is also shown in Figure 23. Several wafers were found to be contaminated with very minor amounts of calcium. This is shown in Figure 24 for one wafer which also had silver contamination as indicated in the figure.

To check for a correlation with electrical parameters, measurements of BV_{CBO} were carried out for a number of devices on each wafer. These measurements were made using a Tektronix transistor curve tracer. Break-down voltages were typically found to lie in the range of 180 to 230 volts. It was of interest to note that the break-down voltages were not stable in time but tended to change by approximately 10 per cent over a period of several minutes. The behavior of most of the transistors checked was such that the break-down voltages initially decreased by a

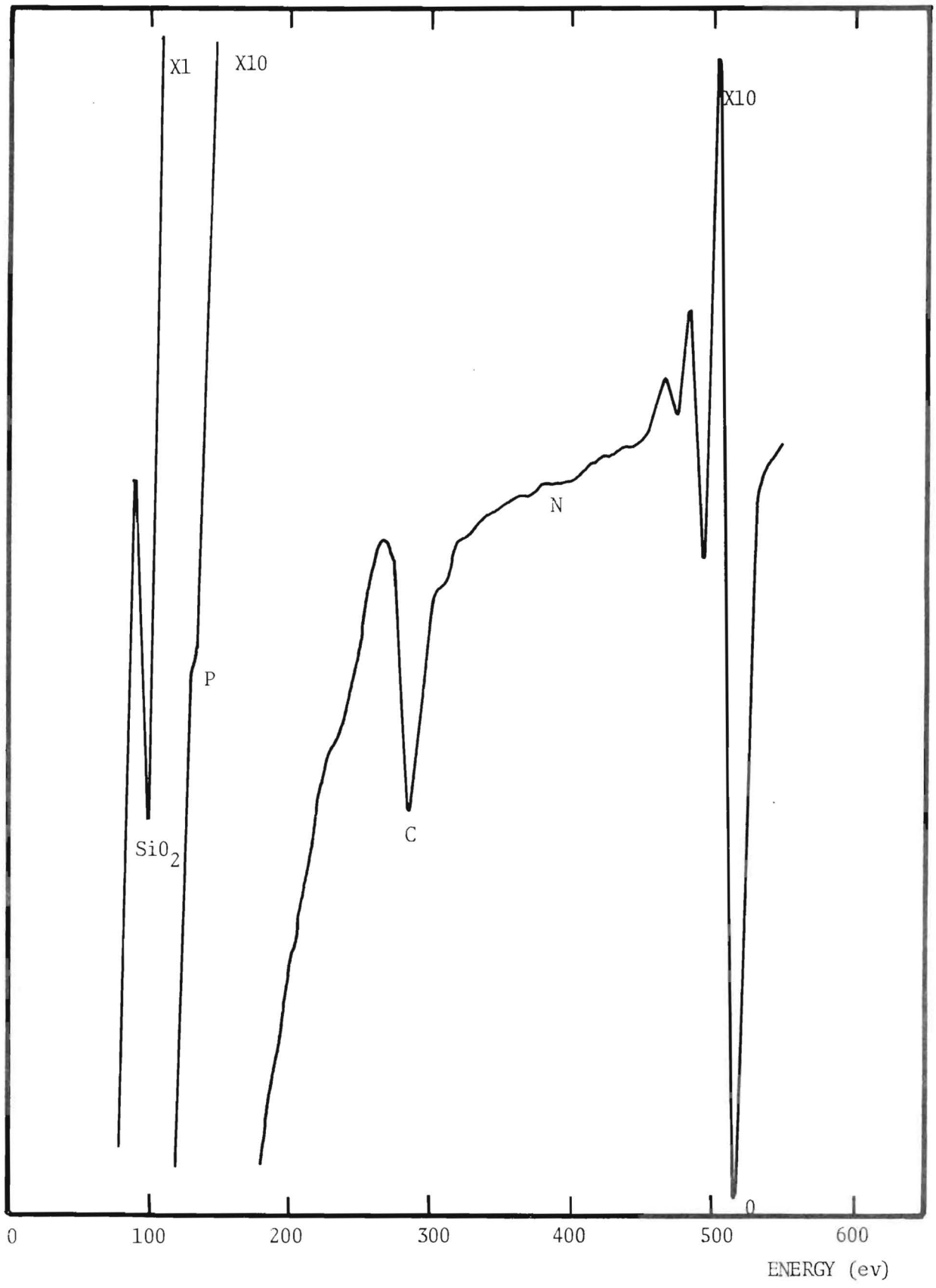

FIGURE 22. TYPICAL WAFER AFTER EMITTER DIFFUSION

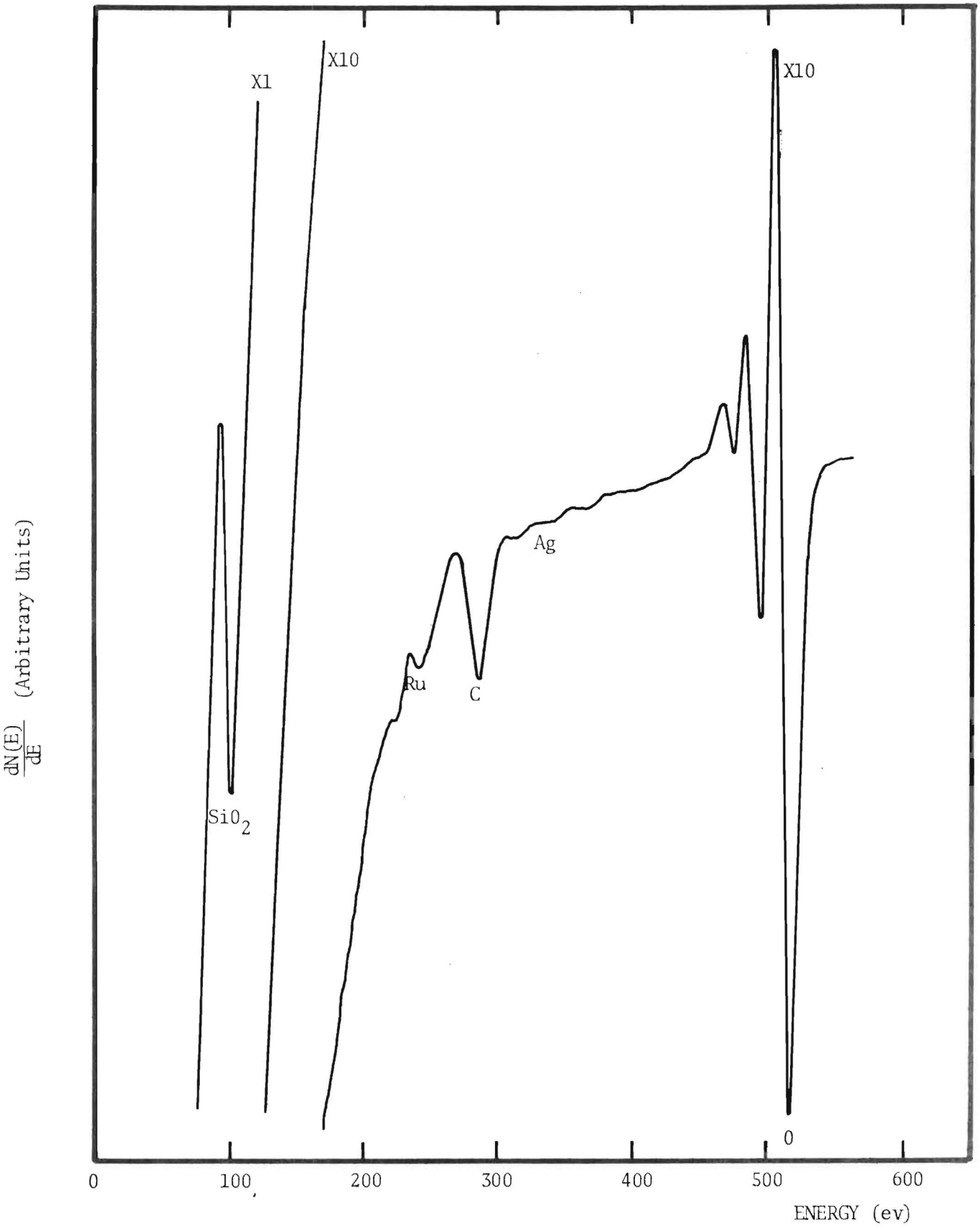

FIGURE 23. WAFER AFTER EMITTER DIFFUSION SHOWING Ru AND Ag CONTAMINATION

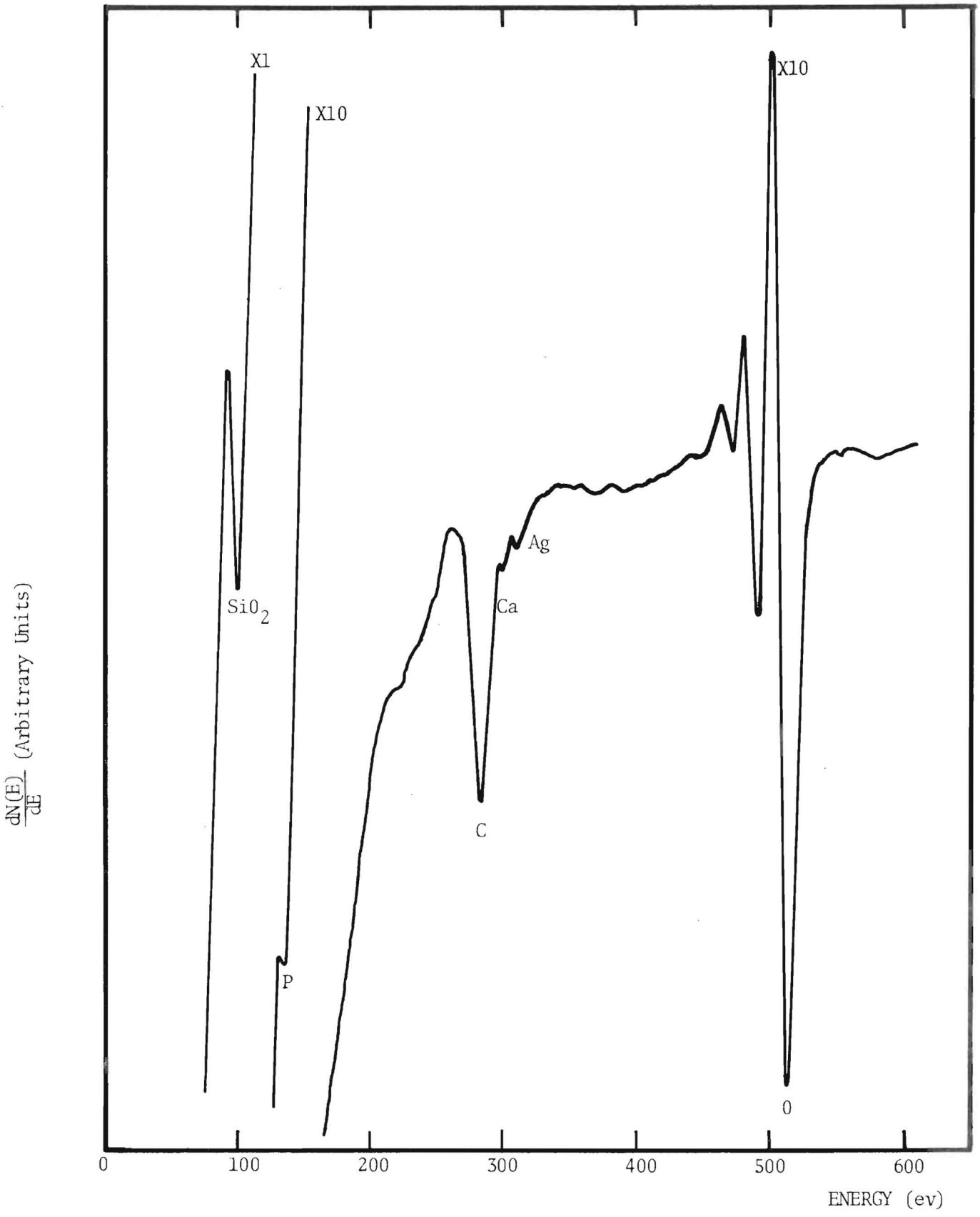

FIGURE 24. WAFER AFTER EMITTER DIFFUSION SHOWING Ca AND Ag CONTAMINATION

small amount and then increased to a final value approximately 20 volts greater than the initial break-down voltages.

The devices checked fell generally into two classes with regard to the "sharpness" of the observed break-down. There was also some division of the wafers in terms of the amount of "walk-away" observed. Six wafers showed average shifts of break-down voltage less than 20 volts while three wafers had average shifts significantly greater than 20 volts. One wafer was found to have very eratic break-down voltages with time for several devices on the wafer and unusually large increases of break-down voltage for others.

There was no correlation between the Auger data, taken after emitter diffusion, and the measured collector-base breakdown characteristics. This was not too surprising since Auger data was not available on the base diffusion for these particular wafers, and one would expect impurities introduced during the formation of the base-collector junction to predominate over impurities introduced at a later step. It would be necessary to characterize a base diffusion and then put the wafer back in the processing line for the emitter diffusion to obtain a definitive test for correlation between Auger data and break-down or "walk-away" phenomena.

E. After Metalization

Ten wafers were examined at this stage with photoresist removed after aluminum masking and cleaning with wafers ready for sintering. A number of impurities were observed including sulfur, boron or chlorine, phosphorous, carbon, oxygen and fluorine. Typical curves are shown in Figures 25 and 26. The Auger spectra are similar except that the carbon is seen to be reduced in Figure 26 and the fluorine increased. One wafer showed unusual concentrations of phosphorous as indicated in

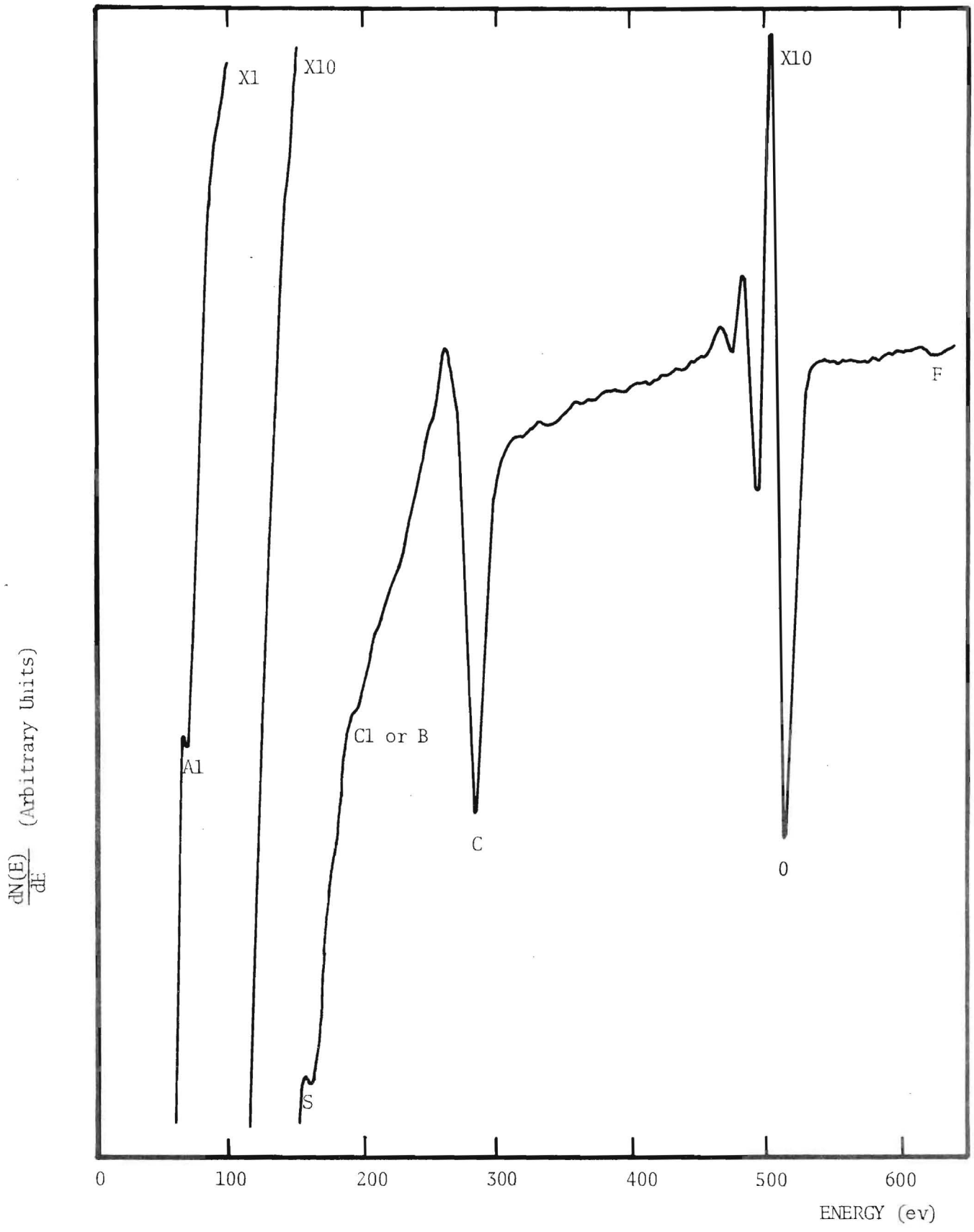

FIGURE 25. TYPICAL WAFER AFTER Al MASK, PHOTORESIST REMOVED

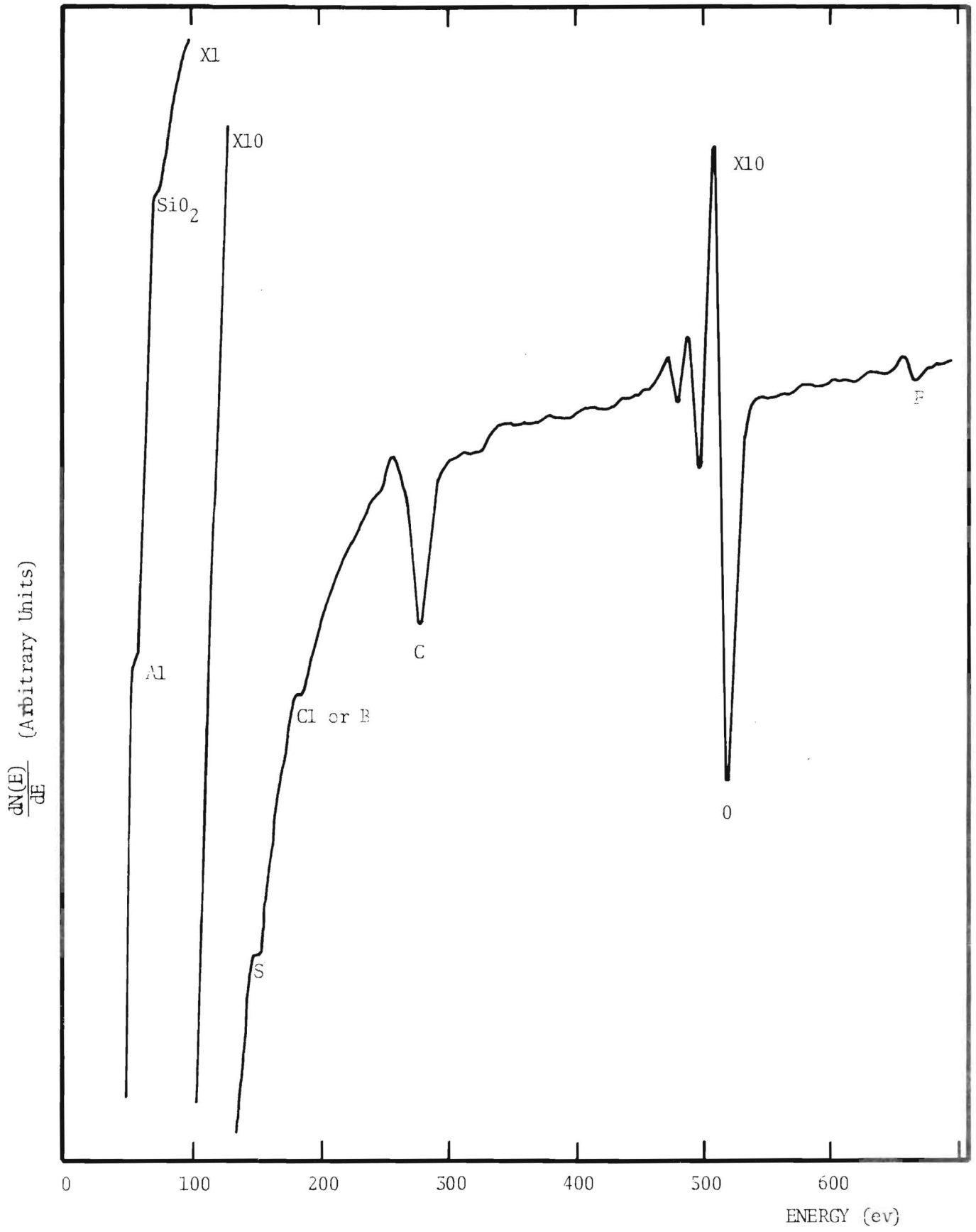

FIGURE 26. WAFER AFTER Al MASK, PHOTORESIST REMOVED SHOWING F CONTAMINATION

Figure 27 and, while all wafers had some sulfur contamination, this contamination was on one wafer found to be excessive as presented in the Auger spectrum of Figure 28.

Again because of the lack of acceptable sputtering capability it was not possible to expose underlying layers for examination for the purpose of correlating with known electronic parameter variations.

F. Completed Devices

The final step examined in the fabrication process was the completed device. Several transistors were mounted on a molybdenum plate for analysis, and a typical Auger spectrum is presented in Figure 29. These devices, which were supplied before bonding of leads, exhibited contamination similar to that reported after metalization. This included impurity concentrations of phosphorous, sulfur, carbon, nitrogen and oxygen. The most outstanding difference was the presence of an additional impurity, calcium. This impurity was present in small quantities on one of the transistors examined and in much larger quantities on two other devices. On these two other units the calcium appeared to dominate the Auger spectrum indicating greater than monolayer average coverage.

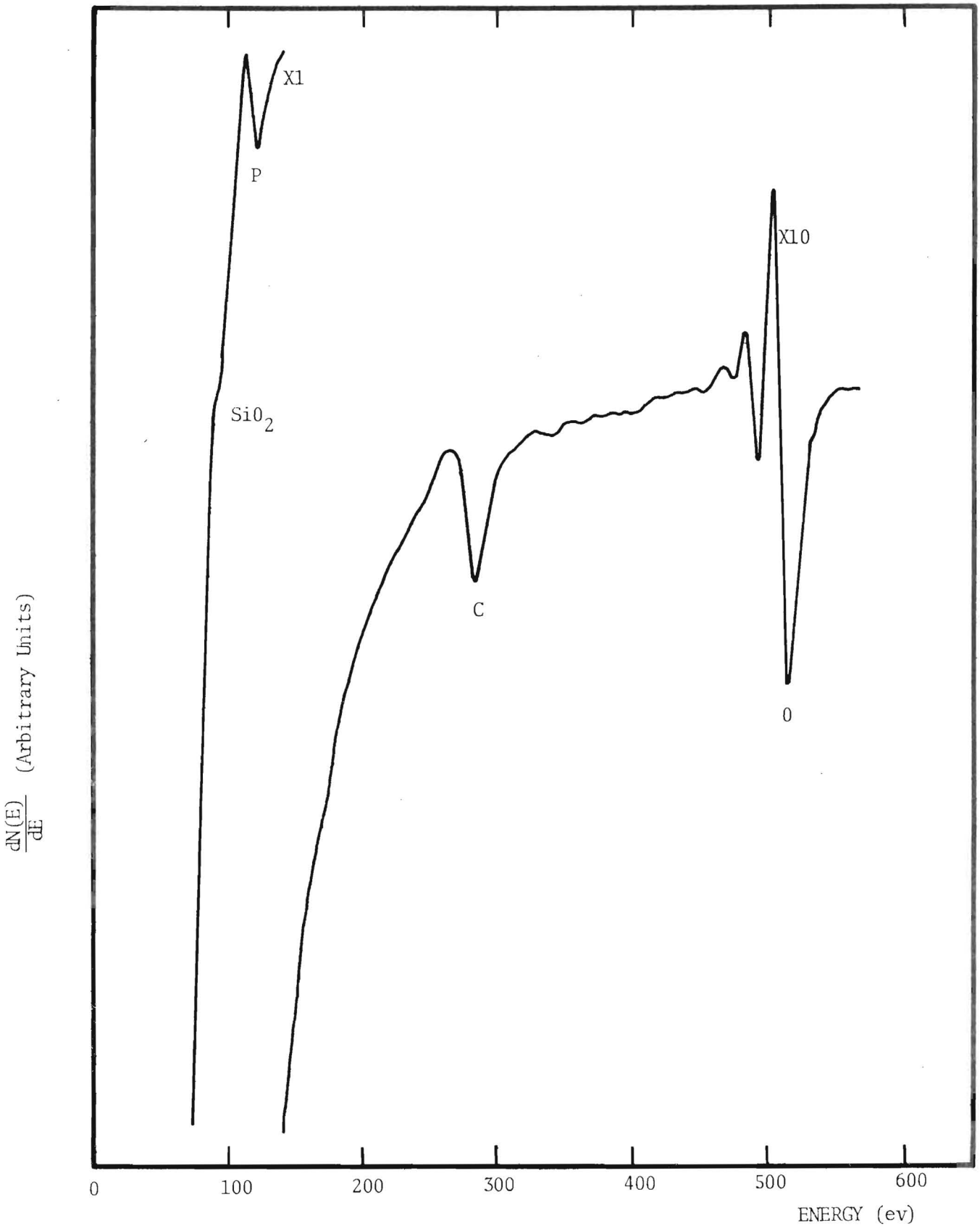

FIGURE 27. WAFER AFTER Al MASK, PHOTORESIST REMOVED SHOWING P CONTAMINATION

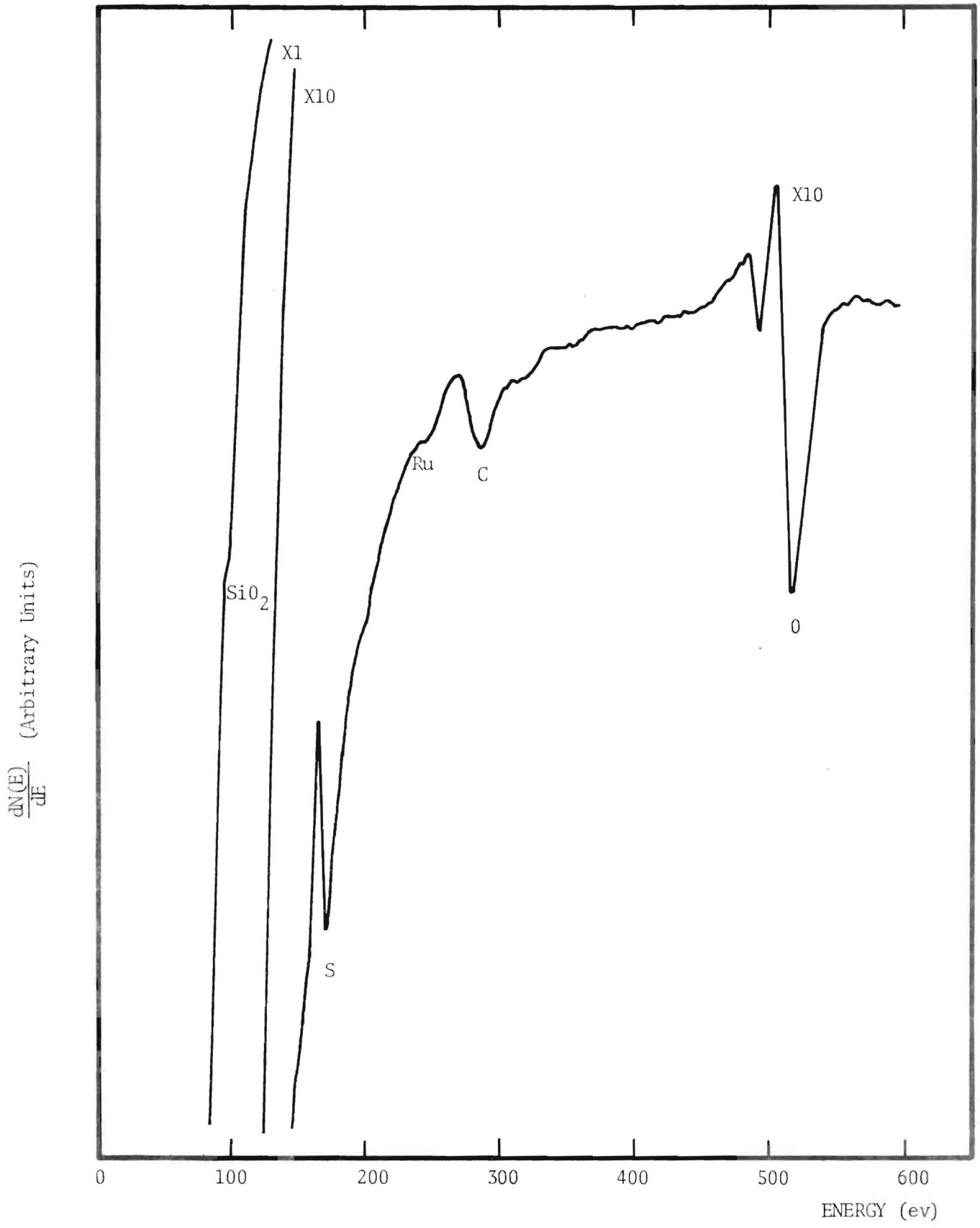

FIGURE 28. WAFER AFTER Al MASK, PHOTORESIST REMOVED SHOWING S CONTAMINATION

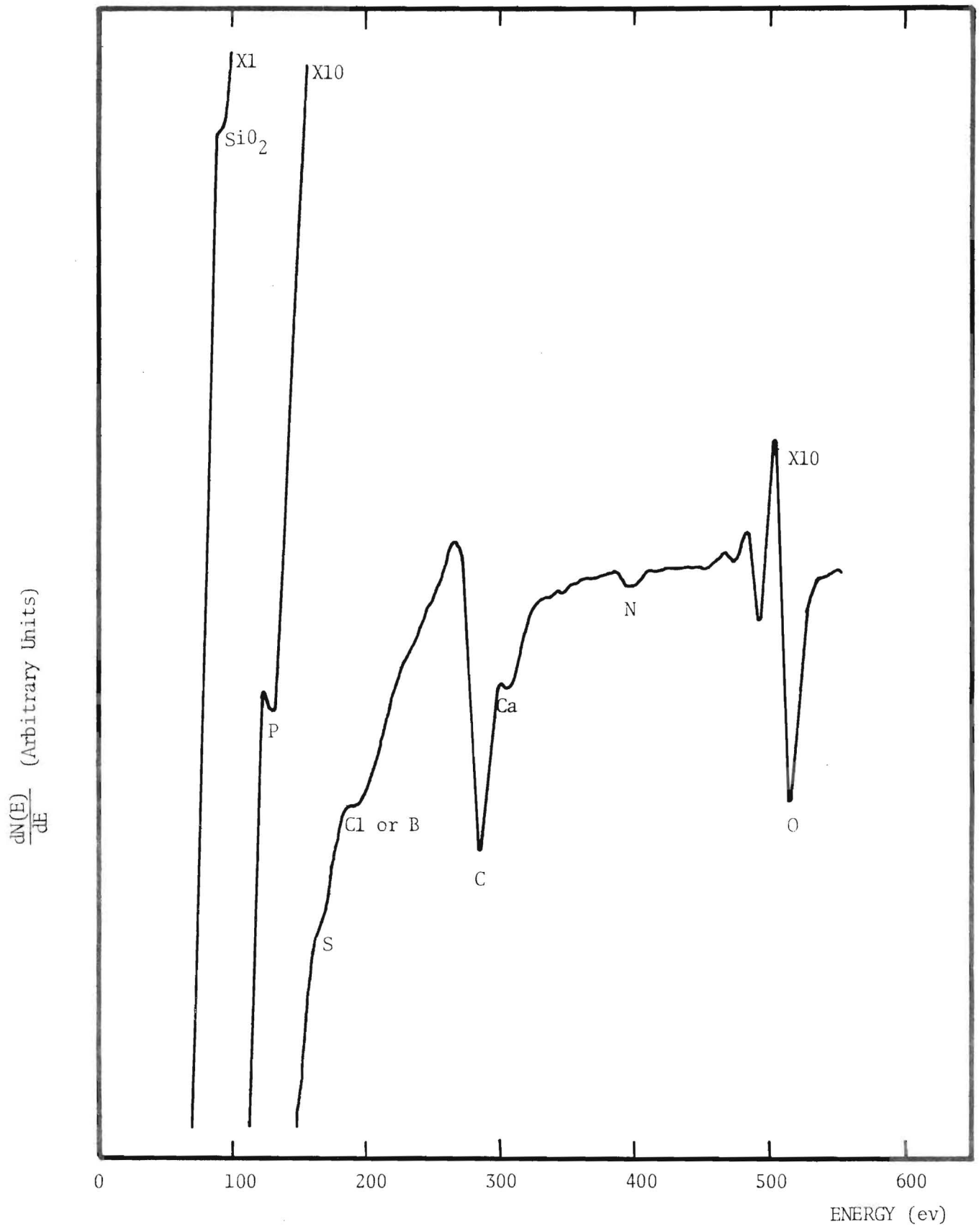

FIGURE 29. TAKEN FROM COMPLETED DEVICE

V. CONCLUSIONS AND RECOMMENDATIONS

During the course of this investigation it has been clearly seen that Auger Spectroscopy has application to impurity problems inherent in the processing of semiconductor devices. The data obtained have provided insight into the nature of the impurities present at the process steps investigated, although the results obtained have certainly been subject to limitations as regards interpretation.

The most serious deficiency in this study has been in the area of reverse sputtering of the wafer samples to expose underlying surfaces for analysis. The desirability of being able to sputter off certain layers of material for determining interfacial impurities is obvious, because this permits a far more comprehensive characterization of the effects of a particular processing operation. This more complete characterization will be essential for making truly meaningful correlations with variations in selected electrical parameters.

The difficulty encountered in attempts to sputter the silicon wafers, as described in earlier progress letters, is that during sputtering there is a redistribution of impurities and a tendency for minute quantities of the sample holder material, in this case molybdenum, to be deposited on the sample surface, thereby masking the impurities of interest. All attempts at general RF-DC sputtering with argon were unsuccessful in this regard. However, this problem should not occur in the case of sputtering with a focused argon beam generated by a low pressure ion source. Such an ion gun has now been developed and is presently undergoing final testing before being added as a permanent sputtering source on the Auger system.

In spite of the limitations mentioned above, the data obtained in this study have proven to be quite useful in evaluating some of the process steps in which difficulty was reported by the manufacturer. For example, the problem of zirconium residue from the polishing operation has been greatly reduced, because the supplier of wafers to the manufacturer has provided an additional process step to insure better removal of the imbedded zirconium oxide particles. It is reported that this additional step has resulted in improved process performance.

The presence of substantial amounts of carbon at many process steps is now being evaluated by the manufacturer in an effort to explain some of the processing problems encountered which may be traceable to carbon in the silicon material. Similarly, the presence of impurities reported after metalization are being considered to determine the connection with occasional irreproducible surface effects.

Correlations between electrical parameters and surface impurities have in no way been complete because of the difficulties mentioned. However, the correlation observed after base diffusion between silver contamination (which appeared after the photoresist step) and diode leakage currents is of interest and suggests the need for a more comprehensive study.

Undoubtedly, this program has demonstrated the usefulness of surface oriented analytical techniques as a means of process evaluation and improvement for semiconductor devices. The data obtained and summarized in this report have identified previously unknown but suspected contaminants causing difficulty in certain process steps. Further, and perhaps most importantly, the results of this study have provided the background data and understanding of this applications area which may now lead to more specific studies designed to better resolve the

problem of correlating process contaminants with meaningful electrical parameters of finished devices.

Respectfully submitted,

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